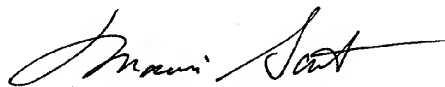


DECLARATION

I, Masami Saito, a Japanese Patent Attorney registered No.12866, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No. 2004-174784 filed on June 11, 2004 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

signed this 4th day of August, 2008.

A handwritten signature in cursive script, appearing to read 'Masami Saito', written in black ink. The signature is fluid and stylized, with a long horizontal stroke extending to the right.

Masami Saito

**PATENT OFFICE
JAPANESE GOVERNMENT**

This is to certify that the annexed is a true copy of the following application
as filed with this Office.

Date of Application: June 11, 2004

Application Number: Japanese Patent Application
No. 2004-174784

The country code and number
of your priority application, JP2004-174784
to be used for filing abroad
under the Paris Convention, is

Applicant(s): CANON KABUSHIKI KAISHA

June 29, 2005

Commissioner,
Patent Office

HIROSHI OGAWA (Seal)

2004-174784

[Name of the document] Patent Application

[Reference No.] 0003897-01

[Date] June 11, 2004

[Addressed to] Commissioner, Patent Office

[International Classification] C12N 9/24

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[Indication of Official Fee]

[Prepayment Ledger No.] 201087

[Amount] 16000

[List of Filed Materials]

[Material] Claims 1

[Material] Specification 1

[Material] Abstract 1

Applicant's Information

Identification No. [000001007]

1. Date of Change: August 30, 1990

(Reason of Change) New Registration

595017850

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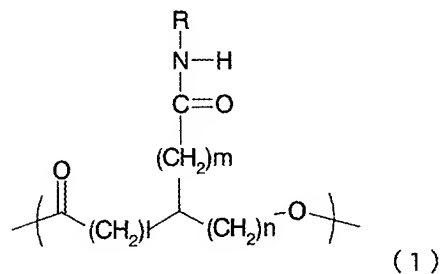
Name: CANON KABUSHIKI KAISHA

[Document] CLAIMS

[Claim 1]

A polyhydroxyalkanoate characterized in that the
 5 polyhydroxyalkanoate comprises one or more units
 represented by the chemical formula (1) in a
 molecule:

[chemical formula 1]

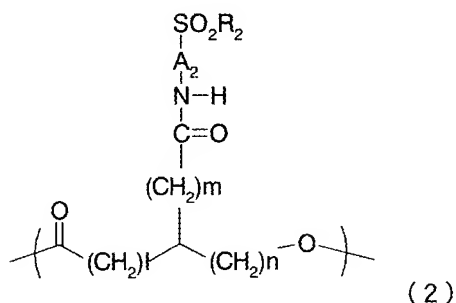


10 wherein R represents $-\text{A}_1-\text{SO}_2\text{R}_1$; R_1 is selected from
 the group consisting of OH, a halogen atom, ONa, OK
 and OR_{1a} ; R_{1a} and A_1 independently represent a group
 having a substituted or unsubstituted aliphatic
 hydrocarbon structure, a substituted or unsubstituted
 15 aromatic ring structure or a substituted or
 unsubstituted heterocyclic structure, respectively; l
 is an integer selected from 1 to 4, n is an integer
 selected from 1 to 4, and m is an integer selected
 from 0 to 8; and when two or more units are present,
 20 R, R_1 , R_{1a} , A_1 , l, m and n mean as above independently
 for every unit.

[Claim 2]

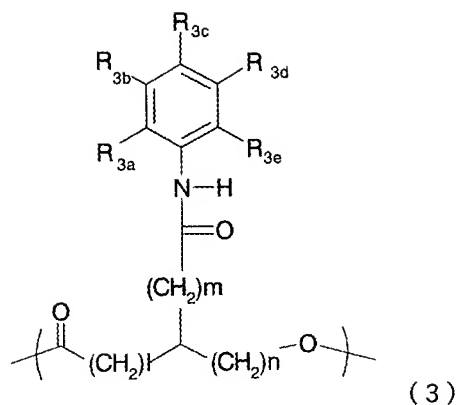
The polyhydroxyalkanoate according to claim 1 characterized in that the polyhydroxyalkanoate comprises one or more units selected from those represented by the chemical formula (2), the chemical formula (3), the chemical formula (4A) or the chemical formula (4B) in a molecule as a unit of chemical formula (1)

[chemical formula 2]



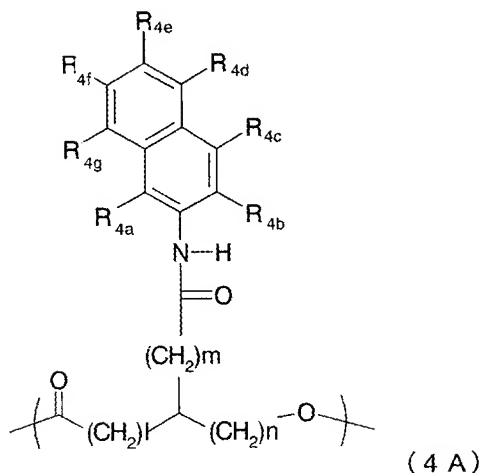
wherein R_2 is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{2a} ; R_{2a} is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; A_2 represents a linear or branched alkylene group having 1 to 8 carbon atoms; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4 and m is an integer selected from 0 to 8; and when two or more units are present, A_2 , R_2 , R_{2a} , l , m and n mean as above independently for every unit.

[chemical formula 3]



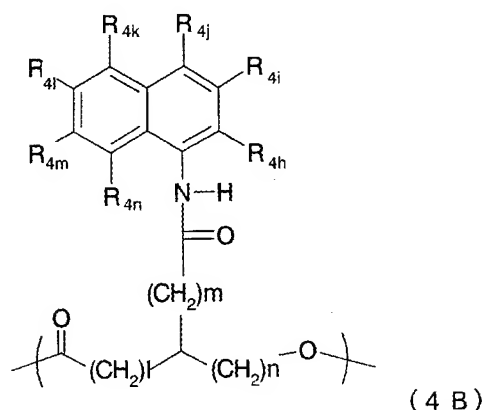
wherein R_{3a} , R_{3b} , R_{3c} , R_{3d} and R_{3e} are independently SO_2R_{3f} wherein R_{3f} is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{3f1} ,
 5 wherein OR_{3f1} is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms,
 10 OH group, NH_2 group, NO_2 group, $COOR_{3g}$ group, wherein R_{3g} represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NHPH group, CF_3 group, C_2F_5 group or C_3F_7 group, wherein Ph represents a phenyl group, respectively, and at least one of these
 15 groups is SO_2R_{3f} ; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, R_{3a} , R_{3b} , R_{3c} , R_{3d} , R_{3e} , R_{3f} , R_{3f1} , R_{3g} , and l , m and n mean as above independently for every
 20 unit

[chemical formula 4]



wherein R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} and R_{4g} are
independently SO_2R_{4o} , wherein R_{4o} is selected from the
5 group consisting of OH, a halogen atom, ONa, OK and
 OR_{4o1} , wherein OR_{4o1} is a linear or branched alkyl
group having 1 to 8 carbon atoms or a substituted or
unsubstituted phenyl group; a hydrogen atom, a
halogen atom, an alkyl group having 1 to 20 carbon
10 atoms, an alkoxy group having 1 to 20 carbon atoms,
OH group, NH_2 group, NO_2 group, $COOR_{4p}$ group, wherein
 R_{4p} represents any of H atom, Na atom and K atom; an
acetamide group, OPh group, NHPH group, CF_3 group,
 C_2F_5 group or C_3F_7 group, wherein Ph represents a
15 phenyl group, respectively, and at least one of these
groups is SO_2R_{4o} ; l is an integer selected from 1 to 4,
n is an integer selected from 1 to 4, and m is an
integer selected from 0 to 8; and when two or more

units are present, R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} , R_{4g} , R_{4o} , R_{4o1} , R_{4p} , and l , m and n mean as above independently for every unit
[chemical formula 5]



5

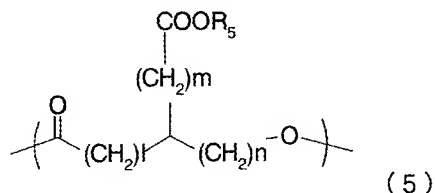
wherein R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} and R_{4n} are independently SO_2R_{4o} , wherein R_{4o} is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{4o1} , wherein OR_{4o1} is a linear or branched alkyl
10 group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, OH group, NH_2 group, NO_2 group, $COOR_{4p}$ group, wherein
15 R_{4p} represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NPh group, CF_3 group, C_2F_5 group or C_3F_7 group, wherein Ph represents a phenyl group, respectively, and at least one of these groups is SO_2R_{4o} ; l is an integer selected from 1 to 4,

n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} , R_{4n} , R_{4o} , R_{4p} , and l, m and n mean as above independently
 5 for every unit.

[Claim 3]

A polyhydroxyalkanoate characterized in that the polyhydroxyalkanoate comprises one or more units represented by the chemical formula (5) in a
 10 molecule:

[chemical formula 6]



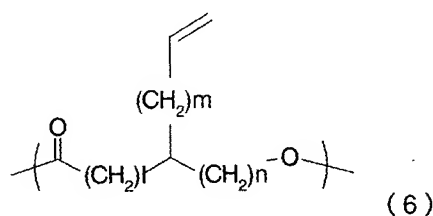
wherein R_5 is hydrogen, a salt forming group or R_{5a} ; R_{5a} is a linear or branched alkyl group having 1 to
 15 12 carbon atoms, an aralkyl group or a substituent having a saccharide; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8; and when l is 1, 3 and 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when l is 2 and n
 20 is 1, 3 and 4, m is an integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when l is 2, n is 2 and m is 0, R_{5a}

is a substituent having a saccharide; and when two or more units are present, R_5 , R_{5a} , and l , m and n mean as above independently for every unit.

[Claim 4]

- 5 A polyhydroxyalkanoate characterized in that the polyhydroxyalkanoate comprises one or more units represented by the chemical formula (6) in a molecule:

[chemical formula 7]



10

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l , m , and n mean as above independently for every unit.

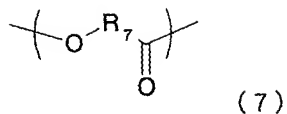
15

[Claim 5]

The polyhydroxyalkanoate according to any one of claims 1 to 4 characterized in that the polyhydroxyalkanoate further comprises one or more units represented by the chemical formula (7) in a molecule:

20

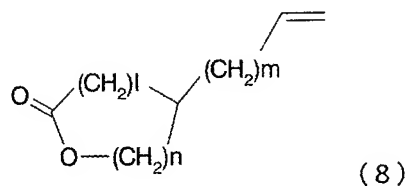
[chemical formula 8]



wherein R₇ is a linear or branched alkylene group having 1 to 11 carbon atoms, an alkyleneoxyalkylene group, wherein each alkylene group is independently
 5 an alkylene group having 1 to 2 carbon atoms, respectively or an alkylidene group having 1 to 5 carbon atoms which may be substituted with aryl; and when two or more units are present, R₇ means as above independently for every unit.

10 [Claim 6]

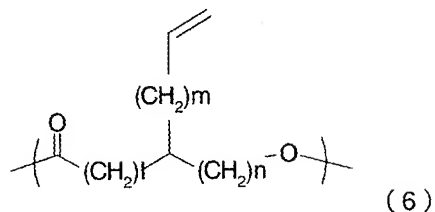
A production method of polyhydroxyalkanoate represented by the chemical formula (6) characterized in that the method comprises a step of polymerizing a compound represented by the chemical formula (8) in
 15 the presence of a catalyst
 [chemical formula 9]



wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer

20 selected from 0 to 8

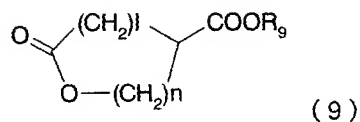
[chemical formula 10]



wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer
 5 selected from 0 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

[Claim 7]

A production method of polyhydroxyalkanoate
 10 represented by the chemical formula (10) characterized in that the method comprises a step of polymerizing a compound represented by the chemical formula (9) in the presence of a catalyst
 [chemical formula 11]

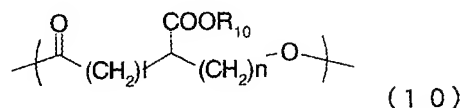


15

wherein R₉ is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l

is 1, 3 or 4, n is an integer selected from 1 to 4,
and when l is 2, n is 1, 3 or 4

[chemical formula 12]

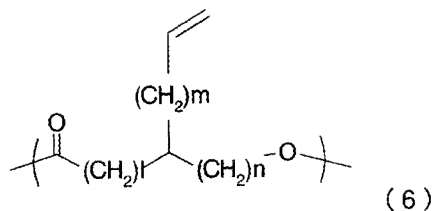


5 wherein R₁₀ is a linear or branched alkyl group
having 1 to 12 carbon atoms or an aralkyl group; l is
an integer selected from 1 to 4, n is an integer
selected from 1 to 4, and when l is 1, 3 or 4, n is
an integer selected from 1 to 4, and when l is 2, n
10 is 1, 3 or 4; and when two or more units are present,
l, n and R₁₀ mean as above independently for every
unit.

[Claim 8]

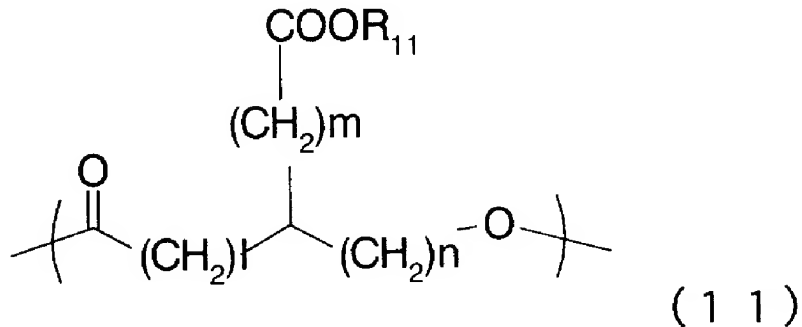
A production method of polyhydroxyalkanoate
15 containing a unit represented by the chemical formula
(11) characterized in that the method comprises a
step of oxidizing a double bond portion of
polyhydroxyalkanoate containing a unit represented by
the chemical formula (6):

20 [chemical formula 13]



wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l , m and n mean as above independently for every unit.

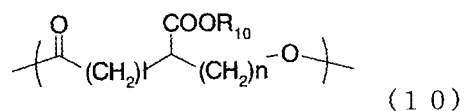
[chemical formula 14]



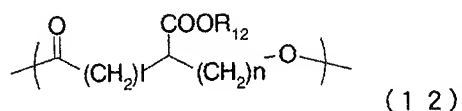
wherein R_{11} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l , m , n and R_{11} mean as above independently for every unit.

[Claim 9]

A production method of polyhydroxyalkanoate
 containing a unit represented by the chemical formula
 (12) characterized in that the method comprises a
 step of hydrolyzing a polyhydroxyalkanoate containing
 5 a unit represented by the chemical formula (10) in
 the presence of acid or alkali, or subjecting a
 polyhydroxyalkanoate containing a unit represented by
 the chemical formula (10) to hydrocracking including
 catalytic reduction:
 10 [chemical formula 15]



wherein R₁₀ is a substituent selected from a linear
 or branched alkyl group having 1 to 12 carbon atoms
 or an aralkyl group; l is an integer selected from 1
 15 to 4, n is an integer selected from 1 to 4, and when
 l is 1, 3 or 4, n is an integer selected from 1 to 4,
 and when l is 2, n is 1, 3 or 4; and when two or more
 units are present, l, n and R₁₀ mean as above
 independently for every unit
 20 [chemical formula 16]

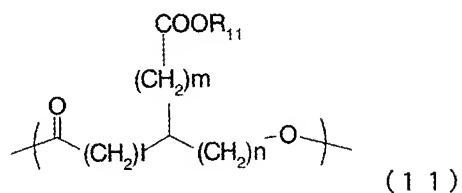


wherein R_{12} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l is 1, 3, and 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3, and 4; and when two or more units are present, l , n and R_{12} mean as above independently for every unit.

[Claim 10]

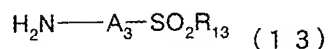
A production method of polyhydroxyalkanoate containing a unit represented by the chemical formula (1) characterized in that the method comprises a step of subjecting a polyhydroxyalkanoate containing a unit represented by the chemical formula (11) and at least one amine compound represented by the chemical formula (13) to condensation reaction:

[chemical formula 17]



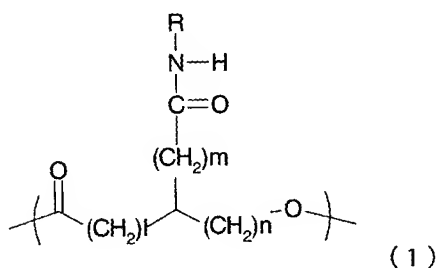
wherein R_{11} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l , m , n and R_{11} mean as above independently for every unit

[chemical formula 18]



wherein R_{13} is selected from the group consisting of
 OH, a halogen atom, ONa, OK and OR_{13a} ; R_{13a} and A_3 are
 5 independently selected from a group having a
 substituted or unsubstituted aliphatic hydrocarbon
 structure, a substituted or unsubstituted aromatic
 ring structure or a substituted or unsubstituted
 heterocyclic structure, respectively; and when two or
 10 more units are present, R_{13} , R_{13a} and A_3 mean as above
 independently for every unit

[chemical formula 19]



wherein R represents $-\text{A}_1-\text{SO}_2\text{R}_1$; R_1 is selected from
 15 the group consisting of OH, a halogen atom, ONa, OK
 and OR_{1a} ; R_{1a} and A_1 independently represent a group
 having a substituted or unsubstituted aliphatic
 hydrocarbon structure, a substituted or unsubstituted
 aromatic ring structure or a substituted or

unsubstituted heterocyclic structure, respectively; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present,
5 R , R_1 , R_{1a} , A_1 , and l , m and n mean as above independently for every unit.

[Document] Specification

[Title of Invention] POLYHYDROXYALKANOATE HAVING
VINYL GROUP, ESTER GROUP, CARBOXYL GROUP AND SULFONIC
ACID GROUP, AND PRODUCTION METHOD THEREOF

5 [Field of the invention]

[0001]

The present invention relates to a novel
polyhydroxyalkanoate and a production method thereof.

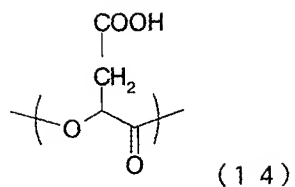
[Background of the invention]

10 [0002]

Biodegradable polymer materials are widely
applied to medical materials, drug delivery systems,
environmentally compatible materials, etc. In recent
years, new functions besides these are further
15 demanded and various researches have been conducted.
Particularly, introducing a chemically modifiable
functional group into a molecule of
polyhydroxyalkanoate represented by polylactic acid
is examined, and there are some reports about a
20 compound to which a carboxyl group, a vinyl group or
the like is introduced. For example, polymalic acid
is known as a polyhydroxyalkanoate having a carboxyl
group in the side chain. Among the polymers of this
polymalic acid, there have been known α -type
25 compounds represented by the chemical formula (14):

[0003]

[chemical formula 1]

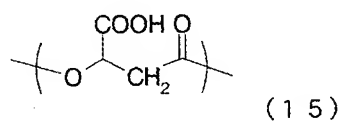


[0004]

and β -type compounds represented by the chemical formula (15):

5 [0005]

[chemical formula 2]



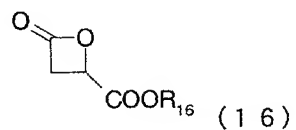
[0006]

which are different in the way of polymer formation.

10 Among these, as for the β -type polymalic acid and its copolymer, a polymer obtained by ring-opening polymerization of benzyl ester of β -malolactone represented by the chemical formula (16):

[0007]

15 [chemical formula 3]



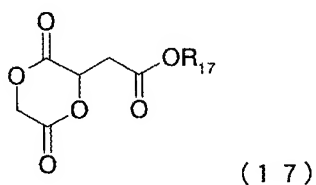
[0008]

(R₁₆: benzyl group) is disclosed in the specification of U.S. Patent No. 4265247 (Patent Document 1). In addition, as for the α -type polymalic acid-glycolic acid copolymer and other copolymers containing

5 hydroxyalkanoic acid including glycolic acid, polymers obtained by copolymerizing a 6-membered cyclic diester monomer represented by the chemical formula (17):

[0009]

10 [chemical formula 4]



[0010]

wherein R₁₇ represents a lower alkyl group such as a methyl group, an ethyl group, n-propyl group, an

15 isopropyl group, and a t-butyl group and a benzyl group, etc., and a glycolide and lactide which are cyclic diesters, a lactone which is an ester by intramolecular ring closure reaction of ω -hydroxycarboxylic acid are disclosed in Japanese

20 Patent Application Laid-Open No. H2-3415 (Patent Document 2).

[0011]

In addition, with regard to a polyhydroxyalkanoate

having a carboxyl group on a side chain, it is disclosed in Macromolecules 2000, 33 (13), 4619-4627 (Nonpatent Document 1) that ring-opening polymerization of 7-oxo-4-oxepane carboxylate ester
5 is conducted to prepare a polymer having an ester group on a side chain, which is further subjected to hydrocracking to prepare a polymer having carboxylic acid on a side chain. Biomacromolecules 2000, 1, 275 (Nonpatent Document 2) discloses a polymer to which
10 benzyloxycarbonyl group is introduced at the α -position methylene group of a carbonyl group in the poly(ϵ -caprolactone) main chain by reacting poly(ϵ -caprolactone) with lithium diisopropylamide and further reacting with benzyl chloroformate.
15 Macromolecular Bioscience 2004, 4, 232 (Nonpatent Document 3) discloses a polymer to which (benzyloxycarbonyl)methyl group is introduced at the α -position methylene group of a carbonyl group in the polylactic acid main chain by reacting polylactic
20 acid with lithium diisopropyl amide and further reacting with benzyl bromoacetate.

With regard to a polyhydroxyalkanoate having a vinyl group on a side chain, Polymeric Materials Science & Engineering 2002, 87, 254 (Nonpatent
25 Document 4) discloses a polymer obtained by ring-opening polymerization of α -allyl(δ -valerolactone). With regard to a polyhydroxyalkanoate having a vinyl

group on a side chain, Polymer Preprints 2002, 43 (2),
727 (Nonpatent Document 5) also discloses a polymer
obtained by ring-opening polymerization of 3,6-
diallyl-1,4-dioxane-2,5-dione which is a 6-membered
5 ring diester monomer.

[0012]

As mentioned above, there have been reported
polymers having new functions imparted by further
introducing a functionality providing structure to a
10 polyhydroxyalkanoate to which a chemically modifiable
functional group has been introduced. In
International Journal of Biological Macromolecules 25
(1999) 265 (Nonpatent Document 6), ring-opening
polymerization of a cyclic dimer of α -malic acid and
15 glycolic acid gives a copolymer of α -type malic acid
and glycolic acid, and a polyester having a carboxyl
group on a side chain is obtained by deprotecting the
obtained polymer. It is described that carboxyl group
of a side chain of this compound was subjected to
20 chemical modification with a tripeptide, the obtained
polymer was evaluated about cellular adhesiveness and
good results were obtained.

[Patent Document 1] U.S. Patent No. 4265247

[Patent Document 2] Japanese Patent Application Laid-
25 Open No. H2-3415

[Nonpatent Document 1] Macromolecules 2000, 33 (13),
4619-4627

[Nonpatent Document 2] Biomacromolecules 2000, 1, 275

[Nonpatent Document 3] Macromolecular Bioscience 2004,
4, 232

[Nonpatent Document 4] Polymeric Materials Science &
5 Engineering 2002, 87, 254

[Nonpatent Document 5] Polymer Preprints 2002, 43 (2),
727

[Nonpatent Document 6] International Journal of
Biological Macromolecules 25 (1999) 265

10

[Disclosure of the invention]

[Problem(s) to be Solved by the Invention]

[0013]

Although it is supposed to be possible to
15 impart a new functionality by introducing a unit
having a carboxyl group or a unit having a vinyl
group which are reactive functional groups into a
molecule and carrying out chemical modification of
the reactive functional group as mentioned above,
20 there have been few reports. Accordingly, the
present invention provides a new polyhydroxyalkanoate
having a reactive functional group in a molecule and
a new polyhydroxyalkanoate having a new function
imparted by performing chemical modification of the
25 polyhydroxyalkanoate having a reactive functional
group and a production method thereof.

[Means for Solving the Problem]

[0014]

Therefore, the present inventors have conducted intensive studies aiming at developing a new polyhydroxyalkanoate having a reactive functional group in a molecule and a new polyhydroxyalkanoate having a new function imparted by performing chemical modification of the polyhydroxyalkanoate having a reactive functional group and consequently achieved the invention shown below.

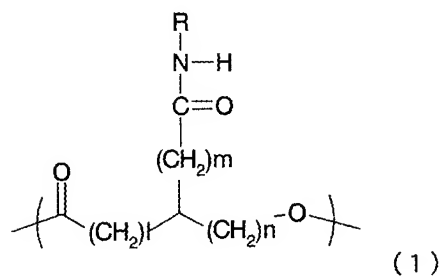
10 [0015]

Polyhydroxyalkanoates according to the present invention include the following.

(1) A polyhydroxyalkanoate comprising one or more units represented by the chemical formula (1) in a molecule:

[0016]

[chemical formula 5]



[0017]

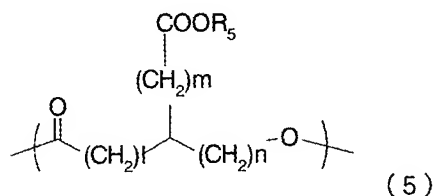
20 wherein R represents $-\text{A}_1-\text{SO}_2\text{R}_1$; R_1 is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{1a} ; R_{1a} and A_1 independently represent a group

having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure, respectively; 1 is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, R, R₁, R_{1a}, A₁, and l, m and n mean as above independently for every unit.

- (2) A polyhydroxyalkanoate comprising one or more units represented by the chemical formula (5) in a molecule:

[0018]

[chemical formula 6]



15

[0019]

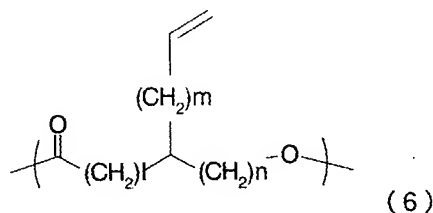
- wherein R₅ is hydrogen, a salt forming group or R_{5a}; R_{5a} is a linear or branched alkyl group having 1 to 12 carbon atoms, an aralkyl group or a substituent having a saccharide; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8; and when l is 1, 3 and 4, n is an integer selected from 1 to 4, and m is an

integer selected from 0 to 8; and when l is 2 and n is 1, 3 and 4, m is an integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when l is 2, n is 2 and m is 0, R_{5a} is a substituting group having a saccharide; and when two or more units are present, R₅, R_{5a}, and l, m and n mean as above independently for every unit.

(3) A polyhydroxyalkanoate comprising one or more units represented by the chemical formula (6) in a molecule:

[0020]

[chemical formula 7]



[0021]

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l, m, and n mean as above independently for every unit.

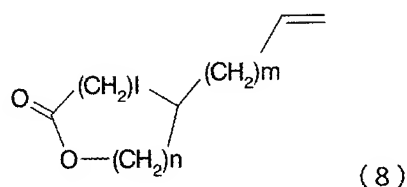
On the other hand, the production method of polyhydroxyalkanoate according to the present invention includes the following.

(A) A production method of polyhydroxyalkanoate

represented by the chemical formula (6) having a step of polymerizing a compound having a unit represented by the chemical formula (8) in the presence of a catalyst.

5 [0022]

[chemical formula 8]

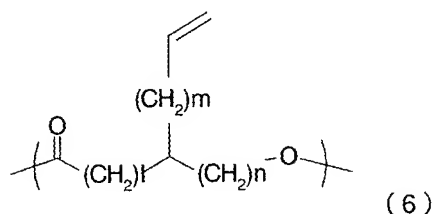


[0023]

wherein l is an integer selected from 1 to 4, n is an
 10 integer selected from 1 to 4, and m is an integer
 selected from 0 to 8.

[0024]

[chemical formula 9]



15 [0025]

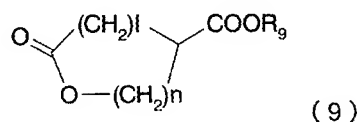
wherein l is an integer selected from 1 to 4, n is an
 integer selected from 1 to 4, and m is an integer
 selected from 0 to 8; and when two or more units are

present, l, m and n mean as above independently for every unit.

(B) A production method of polyhydroxyalkanoate represented by the chemical formula (10) having a
 5 step of polymerizing a compound represented by the chemical formula (9) in the presence of a catalyst.

[0026]

[chemical formula 10]

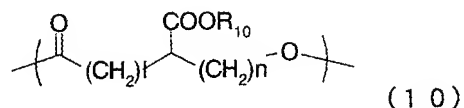


10 [0027]

wherein R₉ is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l
 15 is 1, 3 or 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3 or 4.)

[0028]

[chemical formula 11]



20 [0029]

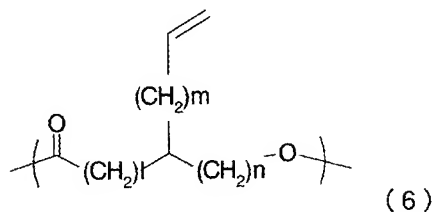
wherein R₁₀ is a substituent selected from a linear

or branched alkyl group having 1 to 12 carbon atoms
 or an aralkyl group; l is an integer selected from 1
 to 4, n is an integer selected from 1 to 4, and when
 l is 1, 3 or 4, n is an integer selected from 1 to 4,
 5 and when l is 2, n is 1, 3 or 4; and when two or more
 units are present, l, n and R₁₀ mean as above
 independently for every unit.

(C) A production method of polyhydroxyalkanoate
 containing a unit represented by the chemical formula
 10 (11) having a step of oxidizing a double bond portion
 of polyhydroxyalkanoate containing a unit represented
 by the chemical formula (6):

[0030]

[chemical formula 12]



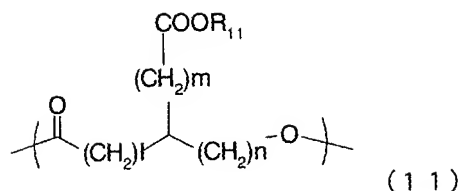
15

[0031]

wherein l is an integer selected from 1 to 4, n is
 an integer selected from 1 to 4, and m is an integer
 selected from 0 to 8; and when two or more units are
 20 present, l, m and n mean as above independently for
 every unit.

[0032]

[chemical formula 13]



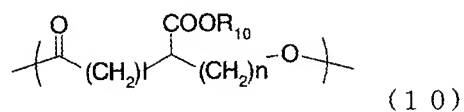
[0033]

wherein R_{11} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l , m , n and R_{11} mean as above independently for every unit.

(D) A production method of polyhydroxyalkanoate containing a unit represented by the chemical formula (12) having a step of hydrolyzing a polyhydroxyalkanoate containing a unit represented by the chemical formula (10) in the presence of acid or alkali, or subjecting a polyhydroxyalkanoate containing a unit represented by the chemical formula (10) to hydrocracking including catalytic reduction:

[0034]

[chemical formula 14]

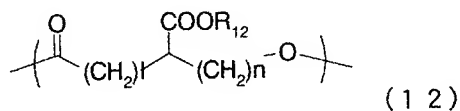


20 [0035]

wherein R_{10} is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when
 5 l is 1, 3 or 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3 or 4; and when two or more units are present, l , n and R_{10} mean as above independently for every unit.

[0036]

10 [chemical formula 15]



[0037]

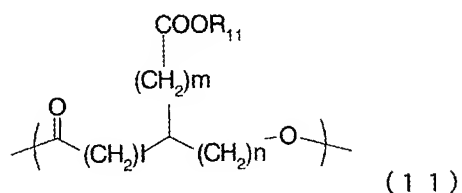
wherein R_{12} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer
 15 selected from 1 to 4, and when l is 1, 3, and 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3, and 4; and when two or more units are present, l , n and R_{12} mean as above independently for every unit.

20 (E) A production method of polyhydroxyalkanoate containing a unit represented by the chemical formula (1) having a step of subjecting a polyhydroxyalkanoate containing a unit represented by the chemical formula (11) and at least one amine

compound represented by the chemical formula (13) to
condensation reaction:

[0038]

[chemical formula 16]



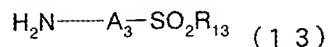
5

[0039]

wherein R_{11} is hydrogen or a salt forming group; l is
an integer selected from 1 to 4, n is an integer
selected from 1 to 4, and m is an integer selected
10 from 0 to 8; and when two or more units are present,
 l , m , n and R_{11} mean as above independently for every
unit.

[0040]

[chemical formula 17]



15

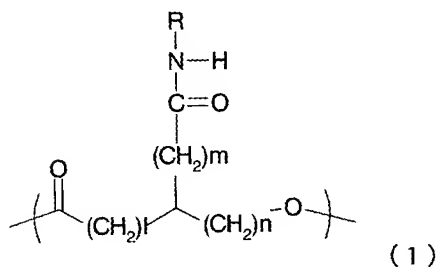
[0041]

wherein R_{13} is selected from the group consisting of
OH, a halogen atom, ONa, OK and OR_{13a} ; R_{13a} and A_3 are
independently selected from a group having a
20 substituted or unsubstituted aliphatic hydrocarbon
structure, a substituted or unsubstituted aromatic

ring structure or a substituted or unsubstituted heterocyclic structure, respectively; and when two or more units are present, R_{13} , R_{13a} and A_3 mean as above independently for every unit.

5 [0042]

[chemical formula 18]



[0043]

wherein R represents $-A_1-SO_2R_1$; R_1 is selected from
 10 the group consisting of OH, a halogen atom, ONa, OK and OR_{1a} ; R_{1a} and A_1 independently represent a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or
 15 unsubstituted heterocyclic structure, respectively; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, R, R_1 , R_{1a} , A_1 , l, m and n mean as above independently
 20 for every unit.

[Best Mode of Carrying Out the Invention]

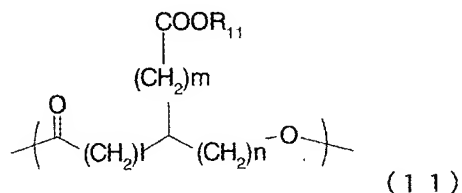
[0044]

Hereinbelow, the present invention is described in more detail referring to preferable embodiments. The target polyhydroxyalkanoate represented by the chemical formula (1) in the present invention can be prepared by reacting polyhydroxyalkanoate containing a unit represented by the chemical formula (11) used as a starting material and at least one aminosulfonic acid compound represented by the chemical formula

10 (13).

[0045]

[chemical formula 19]



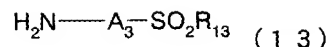
[0046]

15 wherein R_{11} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when two or more units are present, l , m , n and R_{11} mean as above independently for every

20 unit.

[0047]

[chemical formula 20]



[0048]

wherein R_{13} is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{13a} ; R_{13a} and A_3 are
 5 independently selected from a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a substituted or unsubstituted heterocyclic structure, respectively (here, R_{13a} is a
 10 monovalent group having a structure selected from these and A_3 is a divalent group having a structure selected from these); and when two or more units are present, R_{13} , R_{13a} and A_3 mean as above independently for every unit.

15 More in detail, R_{13} is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{13a} . R_{13a} is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group. A_3 represents a group having a linear or
 20 branched substituted or unsubstituted C_1 to C_8 alkylene group, a substituted or unsubstituted phenylene group, a substituted or unsubstituted naphthalene group or a substituted or unsubstituted group having a heterocyclic structure containing one
 25 or more N, S and O. When A_3 is a cyclic structure,

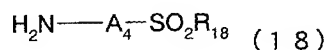
(a) unsubstituted ring(s) may be further condensed.
 Further, when two or more units are present, R_{13} , R_{13a}
 and A_3 mean as above independently for every unit.

[0049]

5 In the case that A_3 is a linear and substituted
 or unsubstituted alkylene group, aminosulfonic acid
 compounds represented by the following chemical
 formula (18) can be mentioned.

[0050]

10 [chemical formula 21]



[0051]

wherein R_{18} is selected from the group consisting of
 OH, a halogen atom, ONa, OK and OR_{18a} ; R_{18a} is a linear
 15 or branched alkyl group having 1 to 8 carbon atoms or
 a substituted or unsubstituted phenyl group; A_4 is a
 linear or branched substituted or unsubstituted C_1 to
 C_8 alkylene group and when it is substituted, it may
 be substituted with an alkyl group having 1 to 20
 20 carbon atoms, an alkoxy group having 1 to 20 carbon
 atoms, etc.

As a compound represented by the chemical
 formula (18), 2-aminoethanesulfonic acid (taurine),
 3-aminopropanesulfonic acid, 4-aminobutanesulfonic
 25 acid, 2-amino-2-methylpropanesulfonic acid, and

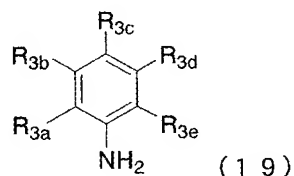
alkaline metal salts and ester compounds thereof, etc.
can be mentioned.

[0052]

In the case that A_3 is a substituted or
5 unsubstituted phenylene group, aminosulfonic acid
compounds represented by the following chemical
formula (19) can be mentioned.

[0053]

[chemical formula 22]



10

[0054]

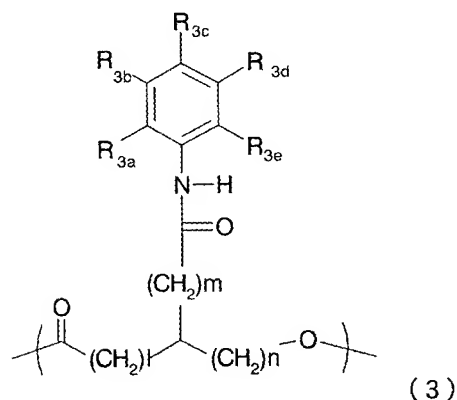
wherein R_{3a} , R_{3b} , R_{3c} , R_{3d} and R_{3e} are independently
selected from the group consisting of SO_2R_{3f} , wherein
 R_{3f} is selected from the group consisting of OH, a
15 halogen atom, ONa, OK and OR_{3f1} wherein OR_{3f1} is a
linear or branched alkyl group having 1 to 8 carbon
atoms or a substituted or unsubstituted phenyl group,
a hydrogen atom, a halogen atom, an alkyl group
having 1 to 20 carbon atoms, an alkoxy group having 1
20 to 20 carbon atoms, OH group and NH_2 group and NO_2
group, $COOR_{3g}$, wherein R_{3g} represents any of H atom,
Na atom and K atom, an acetamide group, OPh group,
NHPh group, CF_3 group, C_2F_5 or C_3F_7 group,

respectively, wherein Ph represents a phenyl group,
and at least one of the groups of these is SO_2R_{3f} ; and
when two or more units are present, R_{3a} , R_{3b} , R_{3c} , R_{3d} ,
 R_{3e} , R_{3f} , R_{3f1} and R_{3g} mean as above independently for
5 every unit.

By using the compound represented by the
chemical formula (19), polyhydroxyalkanoate which
contains in a molecule one or more units represented
by the chemical formula (3) can be obtained.

10 [0055]

[chemical formula 23]



[0056]

wherein R_{3a} , R_{3b} , R_{3c} , R_{3d} , R_{3e} , and l , n and m are
15 similarly defined as the above.

As a compound represented by the chemical
formula (19), p-aminobenzenesulfonic acid (sulfanilic
acid), m-aminobenzenesulfonic acid, o-
aminobenzenesulfonic acid, m-toluidine-4-sulfonic
20 acid, o-toluidine-4-sulfonic acid sodium salt, p-

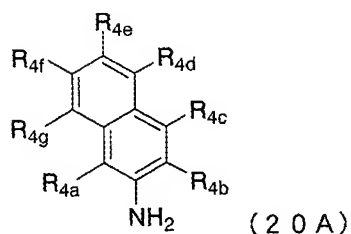
toluidine-2-sulfonic acid, 4-methoxyaniline-2-sulfonic acid, o-anisidine-5-sulfonic acid, p-anisidine-3-sulfonic acid, 3-nitroaniline-4-sulfonic acid, 2-nitroaniline-4-sulfonic acid sodium salt, 4-nitroaniline-2-sulfonic acid sodium salt, 1,5-dinitroaniline-4-sulfonic acid, 2-aminophenol-4-hydroxy-5-nitrobenzenesulfonic acid, 2,4-dimethylaniline-5-sulfonic acid sodium salt, 2,4-dimethylaniline-6-sulfonic acid, 3,4-dimethylaniline-5-sulfonic acid, 4-isopropylaniline-6-sulfonic acid, 4-trifluoromethylaniline-6-sulfonic acid, 3-carboxy-4-hydroxyaniline-5-sulfonic acid, 4-carboxyaniline-6-sulfonic acid and alkaline metal salts and ester compounds thereof, etc. can be mentioned.

[0057]

In the case that A_3 is a substituted or unsubstituted naphthalene group, aminosulfonic acid compounds represented by the following chemical formula (20A) or (20B) can be mentioned.

[0058]

[chemical formula 24]

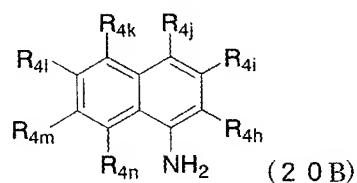


[0059]

wherein R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} and R_{4g} are independently SO_2R_{4o} , wherein R_{4o} is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{4o1} , wherein OR_{4o1} is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, OH group, NH_2 group, NO_2 group, $COOR_{4p}$ group, wherein R_{4p} represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NHPH group, CF_3 group, C_2F_5 group or C_3F_7 group, wherein Ph represents a phenyl group, respectively, and at least one of these groups is SO_2R_{4o} .

[0060]

[chemical formula 25]



[0061]

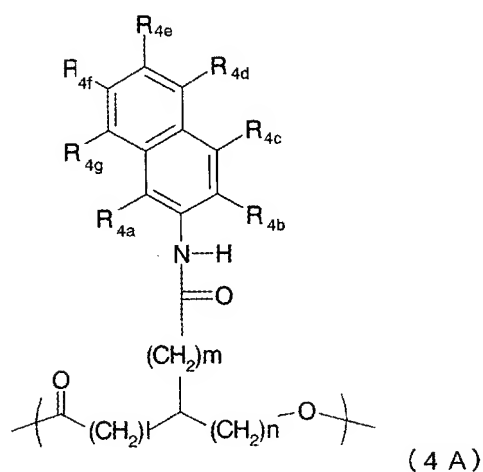
wherein R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} and R_{4n} are independently SO_2R_{4o} wherein R_{4o} is selected from the group consisting of OH, a halogen atom, ONa, OK and OR_{4o1} , wherein R_{4o1} is a linear or branched alkyl group having 1 to 8 carbon atoms or a substituted or

unsubstituted phenyl group; a hydrogen atom, a halogen atom, an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, OH group, NH₂ group, NO₂ group, COOR_{4p} group, wherein
 5 R_{4p} represents any of H atom, Na atom and K atom; an acetamide group, OPh group, NPh group, CF₃ group, C₂F₅ group or C₃F₇ group, wherein Ph represents a phenyl group, respectively, and at least one of these groups is SO₂R_{4o}.

10 Polyhydroxyalkanoate which contains one or more units represented by the chemical formula (4A) or (4B) in a molecule can be obtained by using a compound represented by the chemical formula (20A) or (20B).

15 [0062]

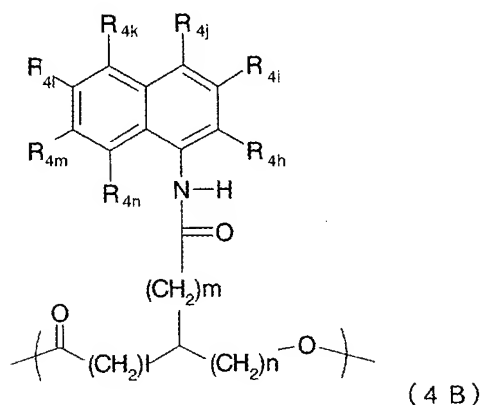
[chemical formula 26]



[0063]

wherein R_{4a} , R_{4b} , R_{4c} , R_{4d} , R_{4e} , R_{4f} and R_{4g} and l , n and m are defined same as above.

[chemical formula 27]



5 [0064]

wherein R_{4h} , R_{4i} , R_{4j} , R_{4k} , R_{4l} , R_{4m} and R_{4n} and l , n and m are defined same as above.

As a compound represented by the chemical formula (20A) or (20B), 1-naphthylamine 5-sulfonic acid, 1-naphthylamine 4-sulfonic acid, 1-naphthylamine 8-sulfonic acid, 2-naphthylamine 5-sulfonic acid, 1-naphthylamine 6-sulfonic acid, 1-naphthylamine-7-sulfonic acid, 1-naphthylamine-2-ethoxy-6-sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 6-amino-1-naphthol-3-sulfonic acid, 1-amino-8-naphthol-2,4-sulfonic acid monosodium salt, 1-amino-8-naphthol-3,6-disulfonic acid monosodium salt, and alkaline metal salts and ester compounds thereof, etc. can be mentioned.

20 [0065]

In the case that A_3 is a substituted or unsubstituted group having a heterocyclic structure containing one or more N, S and O, the heterocyclic structure may be any one of pyridine ring, a
 5 piperazine ring, a furan ring, a thiol ring, etc. As a compound, sulfonic acid such as 2-aminopyridine-6-sulfonic acid and 2-aminopiperazine-6-sulfonic acid and alkaline metal salts and ester compounds thereof, etc. can be mentioned.

10 As a group which binds to a sulfonic acid through an ester bond in the case of sulfonic ester, a group having a substituted or unsubstituted aliphatic hydrocarbon structure, a substituted or unsubstituted aromatic ring structure or a
 15 substituted or unsubstituted heterocyclic structure can be mentioned as above. Furthermore, a linear or branched alkyl group having 1 to 8 carbon atoms, a substituted or unsubstituted phenyl group is preferable. From the viewpoints such as readiness of
 20 esterification, OCH_3 , OC_2H_5 , OC_6H_5 , OC_3H_7 , OC_4H_9 , $OCH(CH_3)_2$, $OCH_2CH_3)_3$, $OC(CH_3)_3$, etc. are more preferable.

[0066]

(Production method of polyhydroxyalkanoate having a
 25 unit represented by the chemical formula (1))

A reaction of polyhydroxyalkanoate containing a unit represented by the chemical formula (11) with an

aminosulfonic acid compound represented by the chemical formula (13) in the present invention is described in detail.

[0067]

5 The amount of the compound represented by the chemical formula (13) used in the present invention is in the range of 0.1 to 50.0 times in mol, preferably 1.0 to 20.0 times in mol for a unit represented by the chemical formula (11) used as a
10 starting material.

[0068]

 There is a condensation reaction by thermal dehydration etc. as a method of generating an amide bond from the carboxylic acid and amine of the
15 present invention. Particularly, a method of activating a carboxylic acid moiety by an activating agent to generate an active acyl intermediate and then reacting it with an amine is effective from the viewpoint of such mild reaction conditions so that
20 ester bonds in the polymer main chain may not be cleaved. As an active acyl intermediate, an acid halide, an acid anhydride, active ester, etc. can be mentioned. Particularly, a method of using
condensing agent and forming an amide bond all over
25 the same reaction space is preferable from the viewpoint of simplification of productive process. If necessary, it is also possible to perform a

condensation reaction with an amine after isolating as an acid halide.

[0069]

As a usable condensing agent, a phosphate
5 condensing agent used for polycondensation of aromatic polyamide, a carbodiimide condensing agent used for peptide synthesis, an acid chloride condensing agent, etc. can be suitably selected based on the combination of the compounds of chemical
10 formulas (13) and (11).

[0070]

As the phosphate condensing agent, a phosphorous acid ester condensing agent, a phosphorus chloride condensing agent, a phosphoric acid
15 anhydride condensing agent, a phosphoric acid ester condensing agent, a phosphoric acid amide condensing agent, etc. can be mentioned.

It is possible to use a condensing agent such as a phosphorous acid ester in the reaction of the
20 present invention. Examples of phosphorous acid ester used on this occasion include triphenyl phosphite, diphenyl phosphite, tri-o-tolyl phosphite, di-o-tolyl phosphite, tri-m-tolyl phosphite, di-m-tolyl phosphite, tri-p-tolyl phosphite, di-p-tolyl
25 phosphite, di-o-chlorophenyl phosphite, tri-p-chlorophenyl phosphite, di-p-chlorophenyl phosphite, trimethyl phosphite, triethyl phosphite, etc.

Particularly, triphenyl phosphite is used preferably.
A metal salt such as lithium chloride and calcium
chloride may be also added for the improvement of
properties such as solubility of and reactivity the
5 polymer.

[0071]

As the carbodiimide condensing agent,
dicyclohexylcarbodiimide (DCC), N-ethyl-N'-3-
dimethylaminopropylcarbodiimide (EDC=WSCI),
10 diisopropylcarbodiimide (DIPC), etc. can be mentioned.
N-hydroxysuccinimide (HONSu), 1-hydroxybenzotriazole
(HOBT) or 3-hydroxy-4-oxo-3,4-dihydro-1,2,3-
benzotriazine (HOObt), etc. may be used in
combination with DCC or WSCI.

15 [0072]

The amount of the condensing agent used is in
the range of 0.1 to 50 times in mol, preferably 1.0
to 20 times in mol for a unit represented by the
chemical formula (11).

20 [0073]

A solvent can be used, if needed, in the
reaction of the present invention. The solvents to
be used include hydrocarbons such as hexane,
cyclohexane and heptane, ketones such as acetone and
25 methyl ethyl ketone, ethers such as dimethyl ether,
diethyl ether, tetrahydrofuran, halogenated
hydrocarbons such as dichloromethane, chloroform,

carbon tetrachloride, dichloroethane and trichloroethane, aromatic hydrocarbons such as benzene and toluene, aprotic polar solvents such as N,N-dimethylformamide, dimethylsulfoxide, 5 dimethylacetamide, and hexamethylphosphoramide, pyridine, pyridine derivatives such as picoline, N-methylpyrrolidone, etc. Pyridine, N-methylpyrrolidone, etc. are used particularly preferably. The amount of the solvent used can be 10 suitably determined depending on the start materials, the kind of base, reaction conditions, etc. Although the reaction temperature is not particularly limited in the method of the present invention, it is usually a temperature in the range of -20°C to the boiling 15 point of the solvent. However, it is preferable to conduct reaction at the optimal temperature for the condensing agent to be used.

[0074]

In the method of the present invention, the 20 range of reaction time is usually 1 to 48 hours. Particularly, 1 to 10 hours is preferable.

[0075]

In the present invention, collection and purification of the target polyhydroxyalkanoate from 25 a reaction liquid containing the thus generated polyhydroxyalkanoate having a unit represented by the chemical formula (1) can be carried out by a normal

method such as distillation. Alternatively, the target polyhydroxyalkanoate represented by the chemical formula (1) can be precipitated by uniformly mixing a solvent such as water, alcohols such as methanol and ethanol, ethers such as dimethyl ether, diethyl ether and tetrahydrofuran with the reaction liquid, and thereby collecting the same.

Polyhydroxyalkanoate having a unit represented by the chemical formula (1) obtained here can be isolated and purified if required. As this isolating and purifying method, there is particularly no restriction and the method of re-precipitating using a solvent insoluble to polyhydroxyalkanoate having a unit represented by the chemical formula (1), method by column chromatography, dialyzing method, etc. can be used.

[0076]

As another production method of the present invention, when R moiety in the chemical formula (1) is $-A_1-SO_3H$, there is a method of performing methyl esterification to convert the R moiety in chemical formula (1) to $-A_1-SO_3CH_3$ using a methyl esterification agent after condensation reaction with an amine. As a methyl esterification agent, those used for methyl esterification of a fatty acid in gas chromatography analysis can be used. As a methyl esterification method, an acid catalyst method such

as hydrochloric acid-methanol method, boron trifluoride-methanol method and sulfuric acid-methanol method, a base catalyst method such as sodium methoxide method, tetramethylguanidine method
5 and trimethylsilyldiazomethane method, etc., can be mentioned. Particularly, trimethylsilyldiazomethane method is preferable since methylation is possible under mild conditions.

[0077]

10 As for the solvent used in the reaction of the present invention, hydrocarbons such as hexane, cyclohexane and heptane, alcohols such as methanol and ethanol, halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride,
15 dichloroethane, and trichloroethane, aromatic hydrocarbons such as benzene and toluene, etc. can be mentioned. Halogenated hydrocarbons are used particularly preferably. The amount of the solvent used can be suitably determined depending on the
20 starting materials, reaction conditions, etc.

Although the reaction temperature is not particularly limited in the method of the present invention, it is usually a temperature in the range of -20°C to 30°C. However, it is preferable to conduct reaction at the
25 optimal temperature for the condensing agent and reagent to be used.

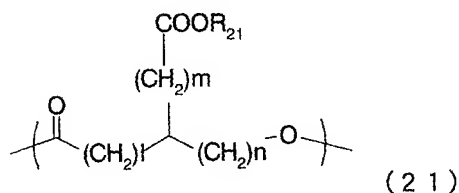
[0078]

In the meantime, among the polyhydroxyalkanoate having a unit represented by the chemical formula (5) of the present invention, a polyhydroxyalkanoate having a unit represented by the chemical formula

5 (21) can be prepared by using a polyhydroxyalkanoate having a unit represented by the chemical formula (22) as a starting material and oxidizing a double bond moiety in the side chain of the polyhydroxyalkanoate.

10 [0079]

[chemical formula 28]



[0080]

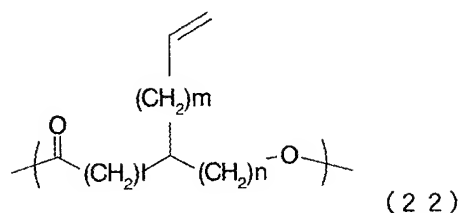
wherein R_{21} is hydrogen or a salt forming group; l is

15 an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8, when l is 1, 3, and 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when l is 2 and n is 1, 3, and 4, m is an

20 integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when two or more units are present, R_{21} , l , m , and n mean as above independently for every unit.

[0081]

[chemical formula 29]



[0082]

5 wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, m is an integer selected from 0 to 8, when l is 1, 3, and 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8; and when l is 2 and n is 1, 3, and 4, m is an integer selected from 0 to 8; and when l is 2 and n is 2, m is an integer selected from 1 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

As a method of carrying out oxidative cleavage
 15 of a carbon-carbon double bond by an oxidizing agent as above to obtain a carboxylic acid, for example, a method using a permanganic acid salt (J. Chem. Soc., Perkin. Trans. 1,806 (1973)), a method using a dichromate (Org. Synth., 4,698 (1963)), a method
 20 using a periodic acid salt (J. Org. Chem., 46, 19 (1981)), a method using nitric acid (Japanese Patent Application Laid-Open No. S59-190945), a method using

ozone (J. Am. Chem. Soc., 81, 4273 (1959)) etc. are known. Macromolecular chemistry, 4,289-293 (2001) also reports a method of obtaining a carboxylic acid by reacting a carbon-carbon double bond at the end of
5 the side chain of polyhydroxyalkanoate produced by microorganisms using potassium permanganate as an oxidizing agent under acidic conditions. The same method can be used also in the present invention.
[0083]

10 As a permanganic acid salt used as an oxidizing agent, potassium permanganate is commonly used. The amount of a permanganic acid salt used may be usually 1 mol equivalent or more and preferably 2 to 10 mol equivalents per one mol of the unit represented by
15 the chemical formula (22), since the oxidative cleavage reaction is a stoichiometric reaction. In order to adjust the reaction system under acidic conditions, various kinds of inorganic acids and organic acids such as sulfuric acid, hydrochloric
20 acid, acetic acid and nitric acid are usually used. However, when acids such as sulfuric acid, nitric acid, hydrochloric acid and the like are used, ester bond in the main chain may be cleaved, which may cause a decrease in the molecular weight. Therefore,
25 it is preferable to use acetic acid. The amount of acid used is usually 0.2 to 2000 mol equivalent and preferably 0.4 to 1000 mol equivalent per one mol of

the unit represented by the chemical formula (22).
When it is not less than 0.2 mol equivalent,
preferable yield will be resulted, and when it is not
more than 2000 mol equivalent, by-product material by
5 decomposition by acid can be reduced, and therefore,
it is preferable to adjust it within the limits as
defined above. Moreover, crown-ethers can be used in
order to promote the reaction. In this case, crown-
ether and permanganic acid salt form a complex, and
10 result in an increased reaction activity. As a
crown-ether, dibenzo-18-crown-6-ether, dicyclo-18-
crown-6-ether and 18-crown-6-ether are generally used.
It is usually preferable to use the crown-ether in an
amount of usually 0.005 to 2.0 mol equivalent, and
15 preferably 0.01 to 1.5 mol equivalent per one mol of
permanganic acid salt.

[0084]

The solvent used in the oxidation reaction of
the present invention is not particularly limited, as
20 long as it is a solvent inactive in the reaction, and,
for example, water, acetone; ethers such as
tetrahydrofuran and dioxane; aromatic hydrocarbons
such as benzene; aliphatic hydrocarbons such as
hexane and heptane; halogenated hydrocarbons such as
25 methyl chloride, dichloromethane and chloroform can
be used. Among these solvents, if the solubility of
polyhydroxyalkanoate is taken into consideration,

halogenated hydrocarbons such as methyl chloride, dichloromethane and chloroform and acetone are preferable.

[0085]

5 The polyhydroxyalkanoate having a unit represented by the chemical formula (22), permanganic acid salt and acid may be placed as a whole together with a solvent from the beginning or each of them may be continuously or intermittently added to the system
10 to proceed the reaction in oxidation reaction of the present invention. In addition, only permanganic acid salt may be previously dissolved or suspended in a solvent, and subsequently polyhydroxyalkanoate and acid may be added to the system continuously or
15 intermittently to proceed the reaction, or only polyhydroxyalkanoate may be previously dissolved or suspended in a solvent, and subsequently permanganic acid salt and acid may be added to the system continuously or intermittently to proceed the
20 reaction. Furthermore, polyhydroxyalkanoate and acid may be placed previously, and subsequently permanganic acid salt may be added to the system continuously or intermittently to proceed the reaction, or permanganic acid salt and acid are
25 placed previously, and subsequently polyhydroxyalkanoate may be added to the system continuously or intermittently to proceed the

reaction, or polyhydroxyalkanoate and permanganic acid salt are placed previously, and subsequently acid may be added to the system continuously or intermittently to proceed the reaction.

5 [0086]

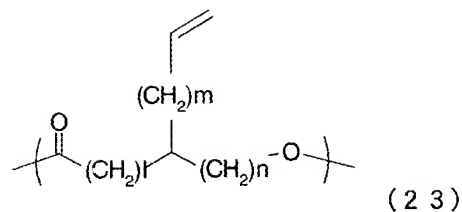
It is suitable to adjust the reaction temperature usually to -40 to 40°C, preferably -10 to 30°C. It is suitable to adjust the reaction time to usually 2 to 48 hours, although it is dependent on
10 the stoichiometric ratio of the unit represented by the chemical formula (22) and permanganic acid salt and the reaction temperature.

[0087]

In addition, polyhydroxyalkanoate containing a
15 unit represented by the chemical formula (24) can be prepared by oxidation reaction from polyhydroxyalkanoate containing a unit represented by the chemical formula (23) by the similar method as the above-described oxidation reaction. This
20 production method is a novel production method.

[0088]

[chemical formula 30]

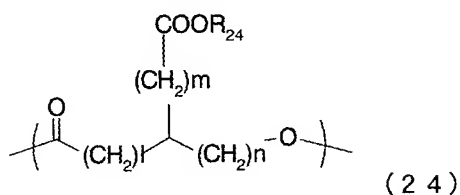


[0089]

wherein l is 2, n is 2, and m is 0.

[0090]

5 [chemical formula 31]



[0091]

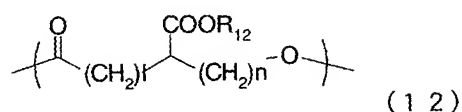
wherein R₂₄ is hydrogen or a salt forming group; l is 2, n is 2, and m is 0.

10 Among the polyhydroxyalkanoates having a unit represented by the chemical formula (5), a polyhydroxyalkanoate having a unit represented by the chemical formula (12) can be also prepared by using polyhydroxyalkanoate having a unit represented by the

15 chemical formula (10) as a starting material by the method of hydrolyzing the side chain ester moiety in the presence of an acid or alkali, or by the method of hydrocracking including catalytic reduction.

[0092]

[chemical formula 32]



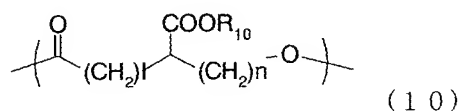
[0093]

5 wherein R_{12} is hydrogen or a salt forming group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l is 1, 3, and 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3, and 4; and when two or more units are

10 present, l , n and R_{12} mean as above independently for every unit.

[0094]

[chemical formula 33]



15 [0095]

wherein R_{10} is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when

20 l is 1, 3 or 4, n is an integer selected from 1 to 4, and when l is 2, n is 1, 3 or 4; and when two or more

units are present, l, n and R₁₀ mean as above independently for every unit.

When a method of hydrolyzing in the presence of an acid or alkali is used, the method can be performed using a solution of an inorganic acid such as hydrochloric acid, sulfuric acid, nitric acid or phosphoric acid, or an organic acid such as trifluoroacetic acid, trichloroacetic acid, p-toluenesulfonic acid and methanesulfonic acid in water or an organic solvent having affinity to water such as methanol, ethanol, tetrahydrofuran, dioxane, dimethylformamide and dimethylsulfoxide, or alternatively using an aqueous solution of an aqueous caustic alkali such as sodium hydroxide and potassium hydroxide or an alkali carbonate such as sodium carbonate and potassium carbonate or an alcoholic solution of metal alkoxide such as sodium methoxide and sodium ethoxide. It is suitable to adjust the reaction temperature usually to 0 to 40°C and preferable to 0 to 30°C. It is suitable to adjust the reaction time usually to 0.5 to 48 hours. However, when hydrolyzation is conducted with an acid or alkali, ester bond in the main chain may be cleaved in any case and may cause decrease in molecular weight.

[0096]

When a method of obtaining a carboxylic acid

using a method of hydrocracking including catalytic reduction is used, the method can be performed as follows. That is, hydrogen is made to act in the presence of a reduction catalyst under normal or
5 increased pressure in a proper solvent at a temperature from -20°C to the boiling point of the solvent used, preferably 0 to 50°C , and catalytic reduction is performed. Examples of the solvent to be used include water, methanol, ethanol, propanol,
10 hexafluoroisopropanol, ethyl acetate, diethyl ether, tetrahydrofuran, dioxane, benzene, toluene, dimethylformamide, pyridine, N-methylpyrrolidone, etc. A mixed solvent of these solvents can also be used. As a reduction catalyst, catalysts such as palladium,
15 platinum, rhodium, etc. by itself or supported on a carrier, or Raney nickel, can be used. It is suitable to adjust the reaction time usually to 0.5 to 72 hours. The thus formed reaction liquid containing a polyhydroxyalkanoate having a unit
20 represented by the chemical formula (10) is collected as a crude polymer by filtering off the catalyst and removing the solvent by distillation etc. The polyhydroxyalkanoate having a unit represented by the chemical formula (10) obtained here can be isolated
25 and purified if required. The method of isolation and purification is not particularly limited and a method of precipitating the polyhydroxyalkanoate

having a unit represented by the chemical formula
(10) using a solvent which does not dissolve the
polyhydroxyalkanoate, a method using column
chromatography, a dialyzing method, etc. can be used.

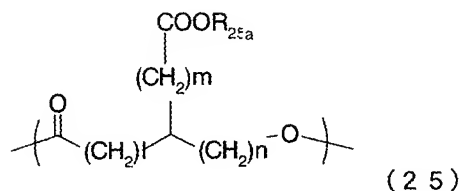
5 However, when catalytic reduction is used, ester bond
in the main chain may be also cleaved and may cause a
decrease in molecular weight.

[0097]

In addition, among the polyhydroxyalkanoates
10 having a unit represented by the chemical formula (5),
a polyhydroxyalkanoate having a unit represented by
the chemical formula (25) can be prepared by
esterifying a polyhydroxyalkanoate having a unit
represented by the chemical formula (11) as a
15 starting material using an esterification agent.

[0098]

[chemical formula 34]



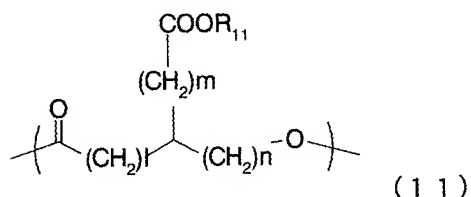
[0099]

20 wherein R_{25a} is a linear or branched alkyl group
having 1 to 12 carbon atoms or an aralkyl group or a
substituent having a saccharide; l is an integer
selected from 1 to 4, n is an integer selected from 1

to 4, m is an integer selected from 0 to 8, and when
 1 is 1, 3, and 4, n is an integer selected from 1 to
 4, and m is an integer selected from 0 to 8; and when
 1 is 2 and n is 1, 3, and 4, m is an integer selected
 5 from 0 to 8; and when 1 is 2 and n is 2, m is an
 integer selected from 1 to 8; and when 1 is 2, n is 2
 and m is 0, R_{25a} is a substituent having a saccharide;
 and when two or more units are present, R_{25a}, and 1, m
 and n mean as above independently for every unit.

10 [0100]

[chemical formula 35]



[0101]

wherein R₁₁ is hydrogen or a salt forming group; 1 is
 15 an integer selected from 1 to 4, n is an integer
 selected from 1 to 4, and m is an integer selected
 from 0 to 8; and when two or more units are present,
 1, m, n and R₁₁ mean as above independently for every
 unit.

20 As an esterification agent used, diazomethane
 and DMF dimethyl acetal can be used. For example,
 polyhydroxyalkanoate having a unit represented by the
 chemical formula (11) reacts easily with DMF dimethyl

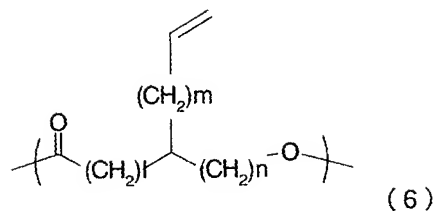
acetal, DMF diethyl acetal, DMF dipropyl acetal, DMF diisopropyl acetal, DMF-n-butyl acetal, DMF-tert-butyl acetal, or DMF dineopentyl acetal, and gives corresponding esters. In addition, an esterified
5 polyhydroxyalkanoate can be obtained by performing a reaction with an alcohol, for example, methanol, ethanol, propanol, isopropyl alcohol, butyl alcohol, sec-butyl alcohol, tert-butyl alcohol, pentyl alcohol, neopentyl alcohol, hexyl alcohol, heptyl alcohol,
10 octyl alcohol, nonyl alcohol, decyl alcohol and lauryl alcohol and saccharides for introducing a group having a saccharide structure, for example, D-glucose, D-fructose and other saccharides following a method using an acid catalyst or a condensing agent
15 such as DCC.

[0102]

A polyhydroxyalkanoate represented by the chemical formula (6) of the present invention can be prepared by carrying out polymerization of an
20 intramolecular closed ring compound of ω -hydroxycarboxylic acid represented by the chemical formula (8) in the presence of a catalyst.

[0103]

[chemical formula 36]

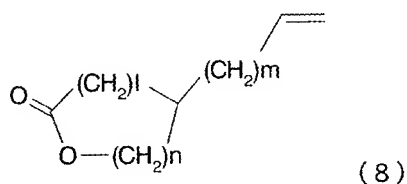


[0104]

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer
 5 selected from 0 to 8; and when two or more units are present, l, m and n mean as above independently for every unit.

[0105]

[chemical formula 37]



10

[0106]

wherein l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and m is an integer selected from 0 to 8.

15

In the production of a polyester containing a unit represented by the chemical formula (6) using an intramolecular closed ring compound of ω-hydroxycarboxylic acid represented by the chemical formula (8) of the present invention, polymerization

method is not particularly limited and, for example, solution polymerization method, slurry polymerization method, mass polymerization method, etc. can be adopted. In addition, when a polymerization solvent
5 is used, the solvent is not particularly limited and, for example, inert solvents such as aliphatic hydrocarbons and cyclic hydrocarbons having 5 to 18 carbon atoms, aromatic hydrocarbons having 6 to 20 carbon atoms, tetrahydrofuran, chloroform, o-
10 dichlorobenzene, dioxane, etc. can be used. Conventional ring-opening polymerization catalysts can be used as a catalyst used for this polymerization. Examples thereof include tin dichloride, tin tetrachloride, stannous fluoride,
15 stannous acetate, stannous stearate, stannous octanoate, stannous oxide, stannic oxide, and other tin salts. In addition, triethoxyaluminum, tri-n-propoxyaluminum, tri-iso-propoxyaluminum, tri-n-butoxyaluminum, tri-iso-butoxyaluminum, aluminium
20 chloride, di-iso-propyl zinc, dimethylzinc, diethylzinc, zinc chloride, tetra-n-propoxytitanium, tetra-n-butoxytitan, tetra-n-butoxytitan, tetra-t-butoxytitan, antimony trifluoride, lead oxide, lead stearate, titanium tetrachloride, boron trifluoride,
25 boron trifluoride-ether complex, triethylamine, tributylamine, etc. can be mentioned.

[0107]

The amount of these catalysts to be used is in the range of 0.0001 to 10% by weight, and preferably in the range of 0.001 to 5% by weight to the total amount of the monomer compound.

5 [0108]

In the present invention, conventional polymerization initiators can be used as a polymerization initiator on the occasion of ring-opening polymerization. Specifically, aliphatic
10 alcohols may be any of mono-, di-, or polyhydric alcohols and may be saturated or unsaturated alcohols. Specifically, monoalcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, nonanol, decanol, lauryl alcohol, myristic alcohol,
15 cetyl alcohol, stearyl alcohol and p-tert-butylbenzyl alcohol, dialcohols such as ethylene glycol, butanediol, hexanediol, nonanediol and tetramethylene glycol, polyhydric alcohols such as glycerol, sorbitol, xylitol, ribitol and erythritol, and methyl
20 lactate, ethyl lactate, etc. can be used. Although there are some differences according to the conditions depending on the alcohol used, these aliphatic alcohols can be usually used at a ratio of 0.01 to 10% by weight to the total amount of the
25 monomer. In the present invention, the temperature of ring-opening polymerization reaction is in the range of 25 to 200°C, preferably in the range of 50

to 200°C, more preferably in the range of 100 to 180°C.

[0109]

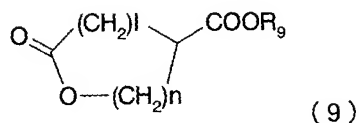
In the present invention, the ring-opening
 5 polymerization reaction may be performed under inert atmosphere such as nitrogen and argon, either reduced or increased pressure, and a catalyst and an alcohol may be added sequentially.

[0110]

10 In addition, the polyhydroxyalkanoate having a unit represented by the chemical formula (10) of the present invention can be prepared by carrying out polymerization of an intramolecular closed ring compound of ω -hydroxycarboxylic acid represented by
 15 the chemical formula (9) in the presence of a catalyst.

[0111]

[chemical formula 38]



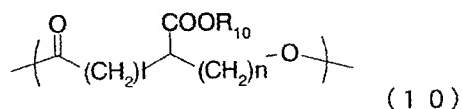
20 [0112]

wherein R₉ is a substituent selected from a linear or branched alkyl group having 1 to 12 carbon atoms or an aralkyl group; l is an integer selected from 1 to 4, n is an integer selected from 1 to 4, and when l

is 1, 3 or 4, n is an integer selected from 1 to 4,
and when l is 2, n is 1, 3 or 4.

[0113]

[chemical formula 39]



5

[0114]

wherein R₁₀ is a substituent selected from a linear
or branched alkyl group having 1 to 12 carbon atoms
or an aralkyl group; l is an integer selected from 1
10 to 4, n is an integer selected from 1 to 4, and when
l is 1, 3 or 4, n is an integer selected from 1 to 4,
and when l is 2, n is 1, 3 or 4; and when two or more
units are present, l and n mean as above
independently for every unit.

15 In the production of a polyester containing a
unit represented by the chemical formula (10) using
an intramolecular closed ring compound of ω-
hydroxycarboxylic acid represented by the chemical
formula (9) of the present invention, polymerization
20 method is not particularly limited and, for example,
solution polymerization method, slurry polymerization
method, mass polymerization method, etc. can be
adopted. In addition, when a polymerization solvent
is used, the solvent is not particularly limited and,

for example, inert solvents such as aliphatic hydrocarbons and cyclic hydrocarbons having 5 to 18 carbon atoms, aromatic hydrocarbons having 6 to 20 carbon atoms, tetrahydrofuran, chloroform, o-
5 dichlorobenzene, dioxane, etc. can be used.
[0115]

In the present invention, conventional ring-opening polymerization catalysts can be used as a catalyst for polymerization. Examples thereof
10 include tin dichloride, tin tetrachloride, stannous fluoride, stannous acetate, stannous stearate, stannous octanoate, stannous oxide, stannic oxide, and other tin salts. In addition, triethoxyaluminum, tri-n-propoxy-aluminum, tri-iso-propoxyaluminum, tri-
15 n-butoxyaluminum, tri-iso-butoxyaluminum, aluminium chloride, di-iso-propyl zinc, dimethylzinc, diethylzinc, zinc chloride, tetra-n-propoxytitanium, tetra-n-butoxytitan, tetra-n-butoxytitan, tetra-t-butoxytitan, antimony trifluoride, lead oxide, lead
20 stearate, titanium tetrachloride, boron trifluoride, boron trifluoride-ether complex, triethylamine, tributylamine, etc. can be mentioned.
[0116]

The amount of these catalysts to be used is in
25 the range of 0.0001 to 10% by weight, and preferably in the range of 0.001 to 5% by weight to the total amount of the monomer compound.

[0117]

In the present invention, conventional polymerization initiators can be used as a polymerization initiator on the occasion of ring-opening polymerization. Specifically, aliphatic alcohols may be any of mono-, di-, or polyhydric alcohols and may be saturated or unsaturated alcohols. Specifically, monoalcohols such as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, nonanol, decanol, lauryl alcohol, myristic alcohol, cetyl alcohol, stearyl alcohol and p-tert-butylbenzyl alcohol, dialcohols such as ethylene glycol, butanediol, hexanediol, nonanediol and tetramethylene glycol, polyhydric alcohols such as glycerol, sorbitol, xylitol, ribitol and erythritol, and methyl lactate, ethyl lactate, etc. can be used. Although there are some differences according to the conditions depending on the alcohol used, these aliphatic alcohols can be usually used at a ratio of 0.01 to 10% by weight to the total amount of the monomer. In the present invention, the temperature of ring-opening polymerization reaction is in the range of 25 to 200°C, preferably in the range of 50 to 200°C, more preferably in the range of 100 to 180°C.

[0118]

In the present invention, the ring-opening

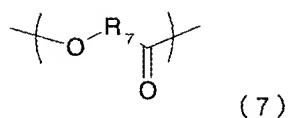
polymerization reaction may be performed under inert atmosphere such as nitrogen and argon, either reduced or increased pressure, and a catalyst and an alcohol may be added sequentially.

5 [0119]

Although the polyhydroxyalkanoate of the present invention is mainly composed of the unit represented by the chemical formula (1), (5) or (6) shown above, it may be also a copolymer to which a
 10 second ingredient etc. is copolymerized in order to change various physical properties such as mechanical properties and decomposition characteristics. For example, a unit represented by the chemical formula (7) can be further contained in a molecule.

15 [0120]

[chemical formula 40]



[0121]

wherein R₇ is a linear or branched alkylene group
 20 having 1 to 11 carbon atoms, an alkyleneoxyalkylene group, wherein each alkylene group is independently an alkylene group having 1 to 2 carbon atoms, respectively, or an alkylidene group having 1 to 5 carbon atoms which may be substituted with aryl; and

when two or more units are present, R_7 means as above independently for every unit.

As an example as the second ingredient, a cyclic diester of α -hydroxycarboxylic acid or a
5 lactone which is an intramolecular closed ring compound of ω -hydroxycarboxylic acid can be copolymerized. Furthermore, specific examples of a cyclic diester of α -hydroxycarboxylic acid include intermolecular cyclic diesters such as glycolide,
10 lactide, α -hydroxybutyric acid, α -hydroxy-isobutyric acid, α -hydroxyvaleric acid, α -hydroxy-isovaleric acid, α -hydroxy- α -methylbutyric acid, α -hydroxycaproic acid, α -hydroxy-isocaproic acid, α -hydroxy- β -methylvaleric acid, α -hydroxyheptanoic acid,
15 mandelic acid, and β -phenyllactic acid. As for the compounds having an asymmetric carbon, any of L-compound, D-compound, racemate and meso compound can be used. The cyclic diester may be also formed from different α -oxy acid molecules. Specifically, a
20 cyclic diester between glycolic acid and lactic acid, and 3-methyl-2,5-diketo-1,4-dioxane etc. can be mentioned. Non-limiting examples of a lactone which is an intramolecular closed ring compound of ω -hydroxycarboxylic acid include β -propiolactone, β -
25 butyrolactone, β -isovalerolactone, β -caprolactone, β -isocaprolactone, β -methyl- β -valerolactone, γ -butyrolactone, γ -valerolactone, δ -valerolactone, δ -

caprolactone, 11-oxydecanoic acid lactone, p-dioxanone, 1,5-dioxepan-2-one.

[0122]

Although the number average molecular weight of
5 polyhydroxyalkanoate obtained by polymerization may vary depending on the conditions such as a type and amount of polymerization catalyst, polymerization temperature and polymerization time, 1,000 to 1,000,000 is preferable.

10 [0123]

The molecular weight of polyhydroxyalkanoate can be measured as a relative molecular weight as well as an absolute molecular weight. It can be simply measured by GPC (gel permeation
15 chromatography), etc. As a specific measuring method by GPC, the above-mentioned polyhydroxyalkanoate is beforehand dissolved in a solvent which can dissolve the polyhydroxyalkanoate, and measurement is performed with a similar mobile phase. As a detector,
20 a differential refraction detector (RI) and an ultraviolet detector (UV) can be used depending on the polyhydroxyalkanoate to be measured. The molecular weight can be determined as a relatively compared value with a standard sample (polystyrene, polymethyl methacrylate, etc.). As a solvent, any
25 solvent which dissolves the polymer such as dimethylformamide (DMF), dimethylsulfoxide (DMSO),

chloroform, tetrahydrofuran (THF), toluene, and hexafluoroisopropanol (HFIP) may be selected. In the case of a polar solvent, measurement can be also performed while a salt is added.

5 [0124]

In the present invention, it is preferable to use a polyhydroxyalkanoate as mentioned above which has a ratio (M_w/M_n) of the weight average molecular weight (M_w) to the number average molecular weight (M_n) measured as mentioned above in the range of 1 to 10.

It should be noted that the reaction solvent, reaction temperature, reaction time, purifying method, etc. in the chemical reaction of the present invention are not limited to the above-mentioned method.

[Examples]

[0125]

Although the present invention is described in more detail referring to Examples given below and, the method of the present invention is not limited only to these Examples.

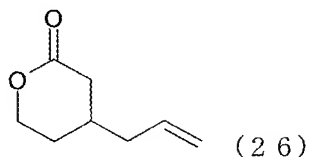
[0126]

(Example 1)

25 (Synthesis of polyester using tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by chemical formula (26))

[0127]

[chemical formula 41]



[0128]

5 1.40 g (0.01 mmol) of tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by the chemical formula (26), 4.0 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.0 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were

10 placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12

15 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 0.53 g of polymer

20 was obtained by carrying out drying under reduced pressure. In order to identify the structure of the obtained polymer, NMR analysis was performed on the following conditions.

<Measurement Apparatus> FT-NMR: Bruker DPX400

Resonant Frequency: ^1H = 400 MHz

<Measurement Conditions> Nuclide Measured: ^1H

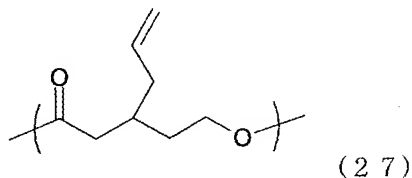
Solvent Used: TMS/ CDCl_3

Measurement Temperature: room temperature

5 Consequently, it was confirmed that the
obtained compound was a polyhydroxyalkanoate which
consists of a unit represented by the following
chemical formula (27).

[0129]

10 [chemical formula 42]



[0130]

The average molecular weight of the obtained
polyhydroxyalkanoate was estimated by gel permeation
15 chromatography (GPC; TOSOH HLC-8220, column; TOSOH
TSK-GEL Super HM-H, solvent; chloroform, polystyrene
conversion). Consequently, the number average
molecular weight, M_n was 6,200, and weight average
molecular weight, M_w was 8,100.

20 [0131]

(Example 2)

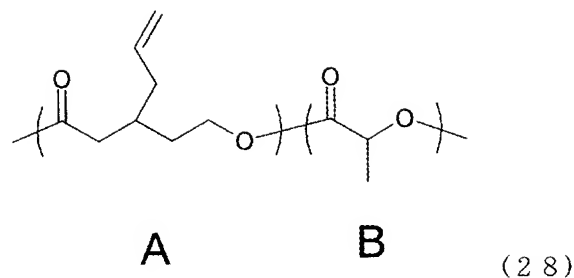
(Synthesis of polyester using tetrahydro-4-(2-
propenyl)-2H-pyran-2-one and L-lactide)

0.28g (2.0 mmol) of tetrahydro-4-(2-propenyl)-

2H-pyran-2-one represented by the chemical formula (26), 1.44 g (10.0 mmol) of L-lactide, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 1.19 g of polymer was obtained by carrying out drying under reduced pressure. In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (28) as a monomer unit. It was also confirmed that the ratios of monomer units were 7 mol% for A unit and 93 mol% for B unit.

[0132]

[chemical formula 43]



[0133]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 21,500, and weight average molecular weight, M_w was 29,900.

10 [0134]

(Example 3)

(Synthesis of polyester using tetrahydro-4-(2-propenyl)-2H-pyran-2-one and L-lactide)

1.40 g (10.0 mmol) of tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by the chemical formula (26), 7.21 g (50.0 mmol) of L-lactide, 2.4 ml of 0.1 M toluene solution of tin octylate (tin 2-ethylhexanoate), 2.4 ml of 0.1 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated

15

20

at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in

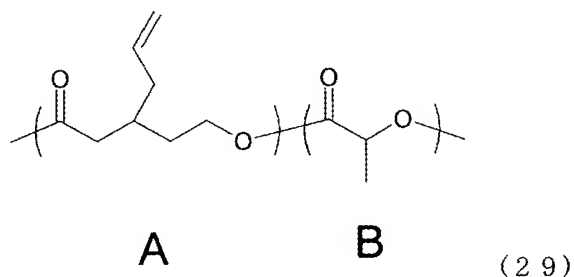
5 methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 6.21 g of polymer was obtained by carrying out drying under reduced pressure. In order to identify the structure of the

10 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (29) as

15 a monomer unit. It was also confirmed that the ratios of monomer units were 8 mol% for A unit and 92 mol% for B unit.

[0135]

[chemical formula 44]



20

[0136]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average
5 molecular weight, M_n was 23,200, and weight average molecular weight, M_w was 32,200.

[0137]

(Example 4)

(Synthesis of polyester using tetrahydro-4-(2-propenyl)-
10 2H-pyran-2-one and mandelide (3,6-diphenyl-1,4-dioxane-2,5-dione))

0.28 g (2.0 mmol) of tetrahydro-4-(2-propenyl)-2H-pyran-2-one represented by the chemical formula (26), 2.68 g (10.0 mmol) of mandelide, 4.8 ml of 0.01
15 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge,
20 it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in
25 methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 1.79 g of polymer was

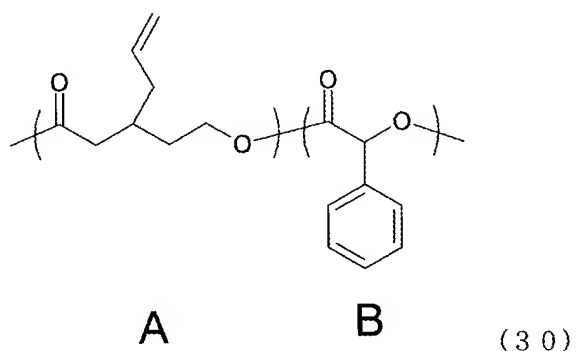
obtained by carrying out drying under reduced pressure.

[0138]

In order to identify the structure of the
 5 obtained polymer, NMR analysis was performed on the
 same conditions as in Example 1 and consequently it
 was confirmed that the obtained compound was a
 polyhydroxyalkanoate copolymer which contains a unit
 represented by the following chemical formula (30) as
 10 a monomer unit. It was also confirmed that the
 ratios of monomer units were 10 mol% for A unit and
 90 mol% for B unit.

[0139]

[chemical formula 45]



15

[0140]

The average molecular weight of the obtained
 polyhydroxyalkanoate was estimated by gel permeation
 chromatography (GPC; TOSOH HLC-8220, column; TOSOH
 20 TSK-GEL Super HM-H, solvent; chloroform, polystyrene

conversion). Consequently, the number average molecular weight, M_n was 18,700, and weight average molecular weight, M_w was 28,800.

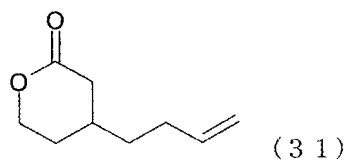
[0141]

5 (Example 5)

(Synthesis of polyester using tetrahydro-4-(2-butenyl)-2H-pyran-2-one represented by chemical formula (31) and δ -valerolactone)

[0142]

10 [chemical formula 46]



[0143]

0.28 g (2.0 mmol) of tetrahydro-4-(3-butenyl)-2H-pyran-2-one represented by the chemical formula (31), 1.00 g (10.0 mmol) of δ -valerolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was

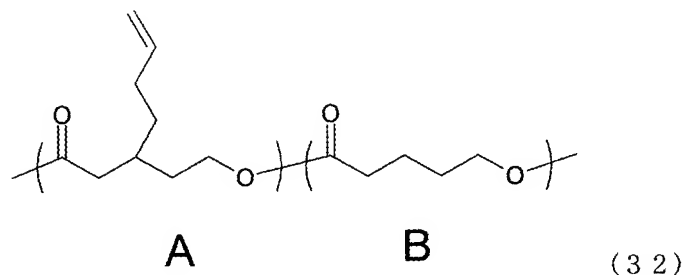
dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 0.89 g of polymer was
 5 obtained by carrying out drying under reduced pressure.

[0144]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the
 10 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (32) as a monomer unit. It was also confirmed that the
 15 ratios of monomer units were 14 mol% for A unit and 86 mol% for B unit.

[0145]

[chemical formula 47]



20 [0146]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average
 5 molecular weight, M_n was 21,000, and weight average molecular weight, M_w was 29,000.

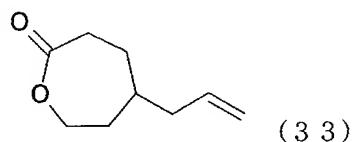
[0147]

(Example 6)

(Synthesis of polyester using 5-(2-propenyl)-2-
 10 oxepanone represented by chemical formula (33) and ϵ -caprolactone)

[0148]

[chemical formula 48]

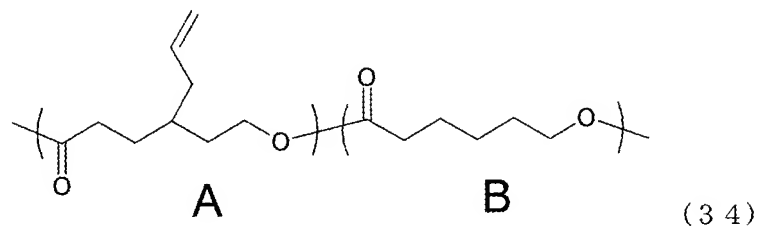


15 [0149]

0.34 g (2.0 mmol) of 5-(2-propenyl)-2-oxepanone represented by the chemical formula (33), 1.14 g (10.0 mmol) of ϵ -caprolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-
 20 ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (34) as a monomer unit. It was also confirmed that the ratios of monomer units were 13 mol% for A unit and 87 mol% for B unit.

[chemical formula 49]



[0152]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH
 5 TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 22,500, and weight average molecular weight, M_w was 32,000.

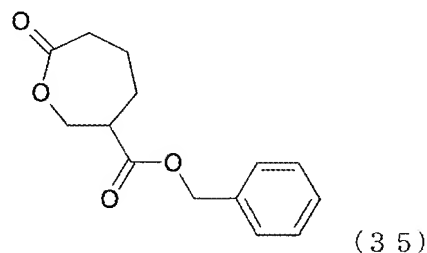
[0153]

10 (Example 7)

(Synthesis of polyester using 7-oxo-3-oxepane carboxylic acid phenylmethyl ester represented by chemical formula (35) and ϵ -caprolactone)

[0154]

15 [chemical formula 50]



[0155]

0.50 g (2.0 mmol) of 7-oxo-3-oxepane carboxylic acid phenylmethyl ester represented by the chemical
 20 formula (35), 1.14 g (10.0 mmol) of ϵ -caprolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene

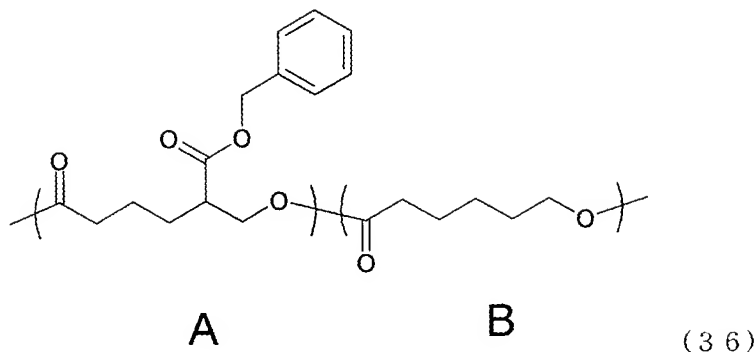
solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated
5 at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform
10 required for dissolving the polymer. The precipitation was collected and 1.23 g of polymer was obtained by carrying out drying under reduced pressure.

[0156]

15 In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit
20 represented by the following chemical formula (36) as a monomer unit. It was also confirmed that the ratios of monomer units were 14 mol% for A unit and 86 mol% for B unit.

[0157]

25 [chemical formula 51]



[0158]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 12,000, and weight average molecular weight, M_w was 16,000.

10 [0159]

1.00 g of the polyhydroxyalkanoate copolymer represented by the chemical formula (36) obtained here was dissolved in 100 ml of a mixed solvent of dioxane-ethanol (75:25), and 0.22 g of 5% palladium/carbon catalyst was added to this, the inside of the reaction system was filled with hydrogen, and the reaction mixture was agitated at room temperature for one day. After the reaction ended, the reaction mixture was filtered with a 0.25 μm membrane filter in order to remove the catalyst,

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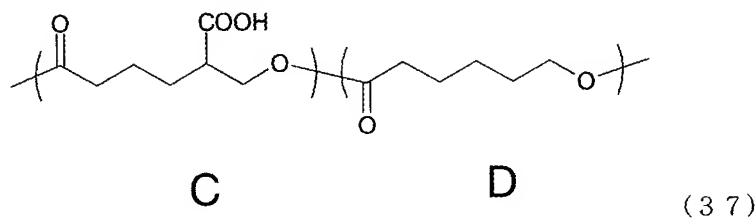
and the reaction solution was collected. After the solution was condensed, it was dissolved in chloroform, re-precipitation was performed using methanol in an amount of 10 times thereof. The
 5 obtained polymer was collected and 0.75 g of polymer was obtained by carrying out drying under reduced pressure.

[0160]

In order to identify the structure of the
 10 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (37) as
 15 a monomer unit. It was also confirmed that the ratios of monomer units were 14 mol% for C unit and 86 mol% for D unit.

[0161]

[chemical formula 52]



20

[0162]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average
 5 molecular weight, M_n was 10,600, and weight average molecular weight, M_w was 14,700.

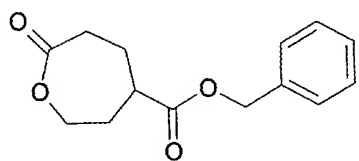
[0163]

(Example 8)

(Synthesis of polyester using 7-oxo-4-oxepane
 10 carboxylic acid phenylmethyl ester represented by chemical formula (38) and ϵ -caprolactone)

[0164]

[chemical formula 53]



(38)

15 [0165]

2.48 g (10.0 mmol) of 7-oxo-4-oxepane carboxylic acid phenylmethyl ester represented by the chemical formula (38), 7.21 g (50.0 mmol) of L-lactide, 2.4 ml of 0.1 M toluene solution of tin
 20 octylate (tin 2-ethylhexanoate), 2.4 ml of 0.1 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced

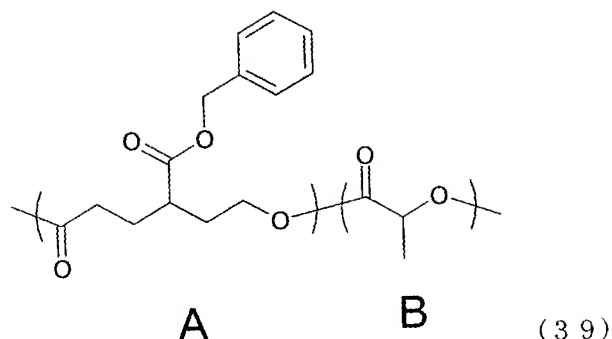
pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-
5 precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 7.08 g of polymer was obtained by carrying out drying under reduced pressure.

10 [0166]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a
15 polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (39) as a monomer unit. It was also confirmed that the ratios of monomer units were 8 mol% for A unit and 92 mol% for B unit.

20 [0167]

[chemical formula 54]



[0168]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 10,300, and weight average molecular weight, M_w was 14,800.

10 [0169]

5.00 g of the polyhydroxyalkanoate copolymer represented by the chemical formula (39) obtained here was dissolved in 500 ml of a mixed solvent of dioxane-ethanol (75:25), and 1.10 g of 5% palladium/carbon catalyst was added to this, the inside of the reaction system was filled with hydrogen, and the reaction mixture was agitated at room temperature for one day. After the reaction ended, the reaction mixture was filtered with a 0.25 μm membrane filter in order to remove the catalyst, and the reaction solution was collected. After the

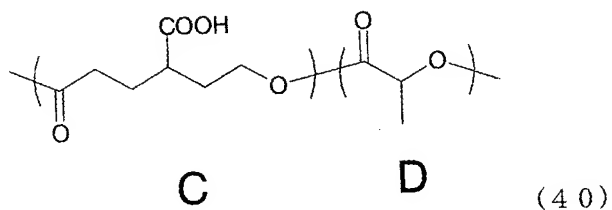
solution was condensed, it was dissolved in chloroform, re-precipitation was performed using methanol in an amount of 10 times thereof. The obtained polymer was collected and 3.70 g of polymer
 5 was obtained by carrying out drying under reduced pressure.

[0170]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the
 10 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (40) as a monomer unit. It was also confirmed that the
 15 ratios of monomer units were 8 mol% for C unit and 92 mol% for D unit.

[0171]

[chemical formula 55]



20 [0172]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation

chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 9,500, and weight average
 5 molecular weight, M_w was 12,900.

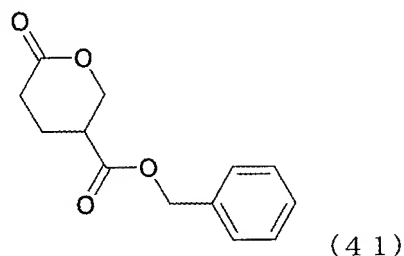
[0173]

(Example 9)

(Synthesis of polyester using tetrahydro-6-oxo-2H-pyran-3-carboxylic acid phenylmethyl ester
 10 represented by chemical formula (41) and mandelide)

[0174]

[chemical formula 56]



[0175]

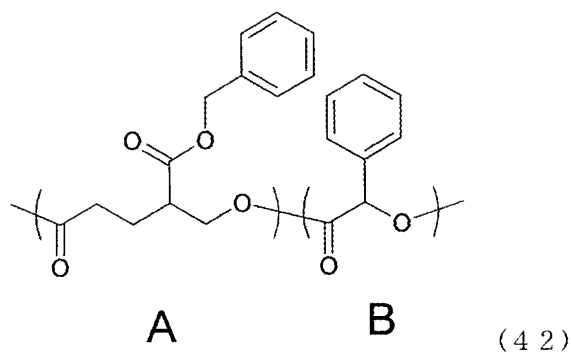
15 0.47g (2.0 mmol) of tetrahydro-6-oxo-2H-pyran-3-carboxylic acid phenylmethyl ester represented by the chemical formula (41), 2.68 g (10.0 mmol) of mandelide, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M
 20 toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour

and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The
5 obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 2.06 g of polymer was obtained by carrying out drying under reduced
10 pressure.

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a
15 polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (42) as a monomer unit. It was also confirmed that the ratios of monomer units were 7 mol% for A unit and 93 mol% for B unit.

20 [0176]

[chemical formula 57]



[0177]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 12,000, and weight average molecular weight, M_w was 16,000.

10 [0178]

1.00 g of the polyhydroxyalkanoate copolymer represented by the chemical formula (42) obtained here was dissolved in 100 ml of a mixed solvent of dioxane-ethanol (75:25), and 0.22 g of 5% palladium/carbon catalyst was added to this, the inside of the reaction system was filled with hydrogen, and the reaction mixture was agitated at room temperature for one day. After the reaction ended, the reaction mixture was filtered with a 0.25 μm membrane filter in order to remove the catalyst,

20

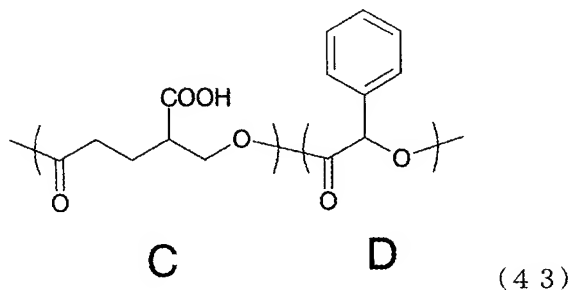
and the reaction solution was collected. After the solution was condensed, it was dissolved in chloroform, re-precipitation was performed using methanol in an amount of 10 times thereof. The
 5 obtained polymer was collected and 0.73 g of polymer was obtained by carrying out drying under reduced pressure.

[0179]

In order to identify the structure of the
 10 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (43) as
 15 a monomer unit. It was also confirmed that the ratios of monomer units were 7 mol% for C unit and 93 mol% for D unit.

[0180]

[chemical formula 58]



20

[0181]

The average molecular weight of the obtained

polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average
 5 molecular weight, M_n was 8,700, and weight average molecular weight, M_w was 12,900.

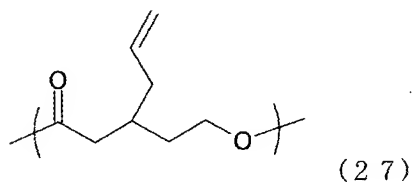
[0182]

(Example 10)

Oxidation reaction of polyhydroxyalkanoate
 10 which consists of a unit represented by chemical formula (27) synthesized in Example 1

[0183]

[chemical formula 59]



15 [0184]

0.50 g of polyhydroxyalkanoate which consists of a unit represented by the chemical formula (27) obtained in Example 1 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was
 20 placed in an ice bath, and 5 ml of acetic acid and 2.83 g of 18-crown-6-ether were added and the mixture was agitated. Next, 2.25 g of potassium permanganate was slowly added on the ice bath, and agitated in an

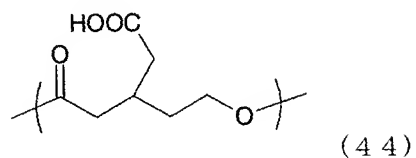
ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.42 g of polymer was obtained by carrying out drying under reduced pressure.

[0185]

20 In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (44) as a monomer unit.

[0186]

[chemical formula 60]



[0187]

The average molecular weight of the obtained
 5 polyhydroxyalkanoate was estimated by gel permeation
 chromatography (GPC; TOSOH HLC-8220, column; TOSOH
 TSK-GEL Super HM-H, solvent; chloroform, polystyrene
 conversion). Consequently, the number average
 molecular weight, M_n was 4,700, and weight average
 10 molecular weight, M_w was 6,200.

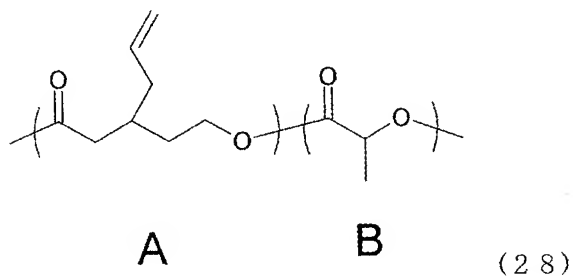
[0188]

(Example 11)

Oxidation reaction of polyhydroxyalkanoate
 which consists of a unit represented by chemical
 15 formula (28) synthesized in Example 2

[0189]

[chemical formula 61]



[0190]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (28) (A: 7 mol%, B: 93 mol%) obtained in
5 Example 2 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.36 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.28 g of potassium permanganate
10 was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen
15 sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer
20 was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an
25 amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.43 g of polymer was obtained by carrying out drying under

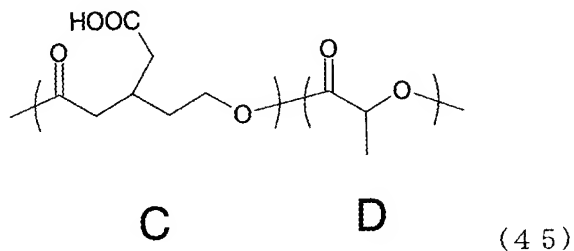
reduced pressure.

[0191]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (45) as a monomer unit.

10 [0192]

[chemical formula 62]



[0193]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 17,400, and weight average molecular weight, M_w was 23,800.

[0194]

In order to calculate the unit of the obtained

polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and
5 the calculation was performed.

[0195]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol
10 added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and
15 the polymer was collected after that. 30 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0196]

In order to identify the structure of the
20 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate represented by the chemical formula (45) was a copolymer having a monomer ratio of 7 mol% for C unit
25 and 93 mol% for D unit.

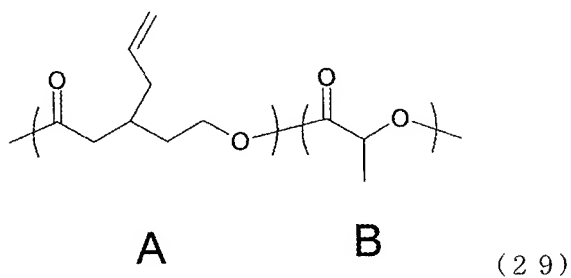
[0197]

(Example 12)

Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (29) synthesized in Example 3

[0198]

5 [chemical formula 63]



[0199]

5.00 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (29) (A: 8 mol%, B: 92 mol%) obtained in Example 3 was added to an eggplant flask and dissolved with 300 ml of acetone added. This was placed in an ice bath, and 50 ml of acetic acid and 4.09 g of 18-crown-6-ether were added and the mixture was agitated. Next, 3.26 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 600 ml of ethyl acetate was added after the reaction ended, and 450 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N

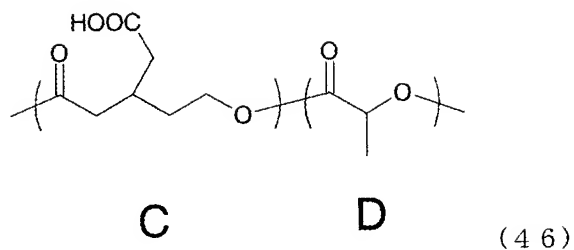
hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next,
5 polymer was collected, after washed with 500 ml of water, 500 ml of methanol and further with 500 ml of water 3 times. Next, it was dissolved in 30 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving
10 the polymer. The precipitation was collected and 4.38 g of polymer was obtained by carrying out drying under reduced pressure.

[0200]

In order to identify the structure of the
15 obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (46) as
20 a monomer unit.

[0201]

[chemical formula 64]



[0202]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 19,800, and weight average molecular weight, M_w was 27,900.

10 [0203]

In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and the calculation was performed.

[0204]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at

room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and the polymer was collected after that. 30 mg of
5 polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0205]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the
10 same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate represented by the chemical formula (46) was a copolymer having a monomer ratio of 8 mol% for C unit and 92 mol% for D unit.

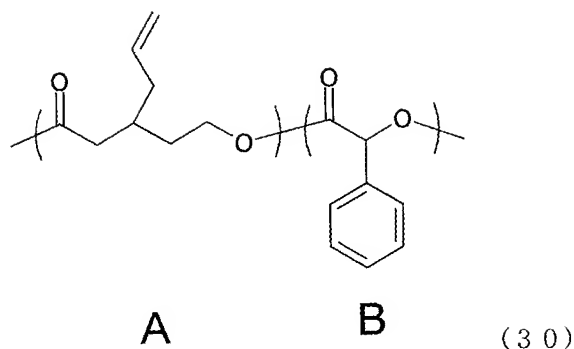
15 [0206]

(Example 13)

Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (30) synthesized in Example 4

20 [0207]

[chemical formula 65]



[0208]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (30) (A: 10 mol%, B: 90 mol%) obtained in

5 Example 4 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.29 g of 18-crown-6-ether were added and the mixture

10 was agitated. Next, 0.23 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml

15 of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid.

20 After the organic layer was collected, crude polymer

was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.41 g of polymer was obtained by carrying out drying under reduced pressure.

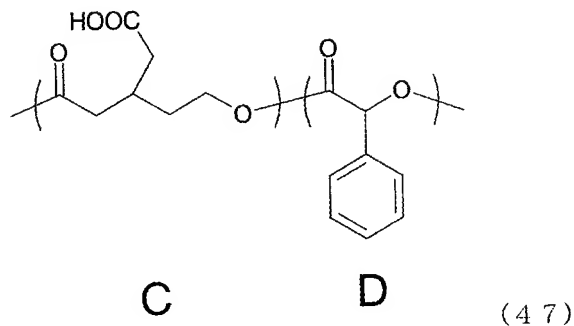
10 [0209]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (47) as a monomer unit.

15

[0210]

[chemical formula 66]



[0211]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH
5 TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 15,500, and weight average molecular weight, M_w was 20,300.

[0212]

10 In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and
15 the calculation was performed.

[0213]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol
20 added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and
25 the polymer was collected after that. 28 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0214]

NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate represented by the chemical formula (47) was a copolymer having a monomer ratio of 10 mol% for C unit and 90 mol% for D unit.

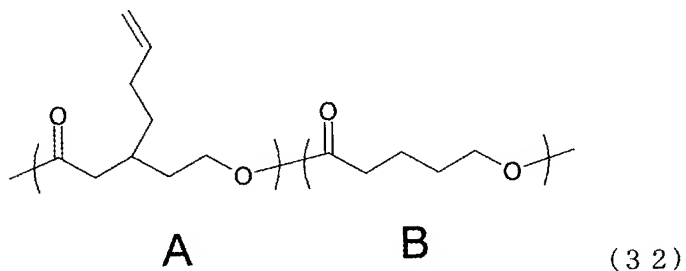
[0215]

(Example 14)

10 Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (32) synthesized in Example 5

[0216]

[chemical formula 67]



15

[0217]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (32) (A: 14 mol%, B: 86 mol%) obtained in Example 5 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and

20

0.52 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.42 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room
5 temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N
10 hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of
15 water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.43 g
20 of polymer was obtained by carrying out drying under reduced pressure.

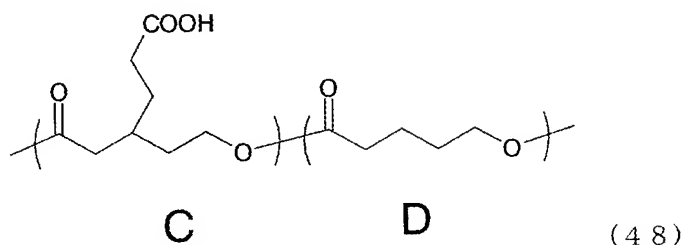
[0218]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the
25 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit

represented by the following chemical formula (48) as a monomer unit.

[0219]

[chemical formula 68]



5

[0220]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 17,900, and weight average molecular weight, M_w was 24,500.

[0221]

In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and the calculation was performed.

20

[0222]

30 mg of the target polyhydroxyalkanoate was

added to 100 ml-volume eggplant flask and dissolved
with 2.1 ml of chloroform and 0.7 ml of methanol
added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-
hexane solution was added to this, and agitated at
5 room temperature for 1 hour. After the reaction
ended, the solvent was removed and the polymer was
collected. It was washed with 50 ml of methanol and
the polymer was collected after that. 29 mg of
polyhydroxyalkanoate was obtained by carrying out
10 drying under reduced pressure.

[0223]

NMR analysis was performed on the same
conditions as in Example 1 and consequently it was
confirmed that the obtained polyhydroxyalkanoate
15 represented by the chemical formula (48) was a
copolymer having a monomer ratio of 13 mol% for C
unit and 87 mol% for D unit.

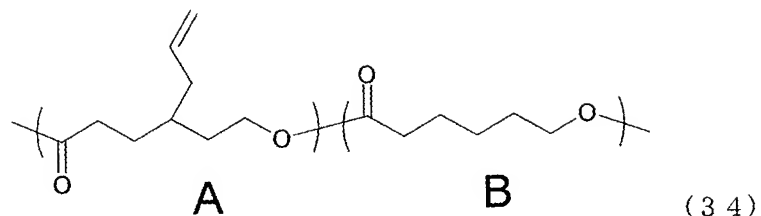
[0224]

(Example 15)

20 Oxidation reaction of polyhydroxyalkanoate
which consists of a unit represented by chemical
formula (34) synthesized in Example 6

[0225]

[chemical formula 69]



[0226]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (34) (A: 13 mol%, B: 87 mol%) obtained in Example 6 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.43 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.34 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of

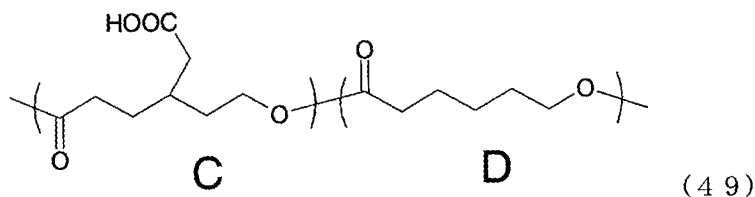
water, 50 ml of methanol and further with 50 ml of water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.44 g of polymer was obtained by carrying out drying under reduced pressure.

[0227]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (49) as a monomer unit.

[0228]

[chemical formula 70]



[0229]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH

TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average molecular weight, M_n was 18,900, and weight average molecular weight, M_w was 27,600.

5 [0230]

In order to calculate the unit of the obtained polyhydroxyalkanoate furthermore, carboxyl groups at the end of the side chains of the polyhydroxyalkanoate were subjected to methyl esterification using trimethylsilyldiazomethane and the calculation was performed.

[0231]

30 mg of the target polyhydroxyalkanoate was added to 100 ml-volume eggplant flask and dissolved with 2.1 ml of chloroform and 0.7 ml of methanol added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution was added to this, and agitated at room temperature for 1 hour. After the reaction ended, the solvent was removed and the polymer was collected. It was washed with 50 ml of methanol and the polymer was collected after that. 28 mg of polyhydroxyalkanoate was obtained by carrying out drying under reduced pressure.

[0232]

25 NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained polyhydroxyalkanoate

represented by the chemical formula (49) was a copolymer having a monomer ratio of 12 mol% for C unit and 88 mol% for D unit.

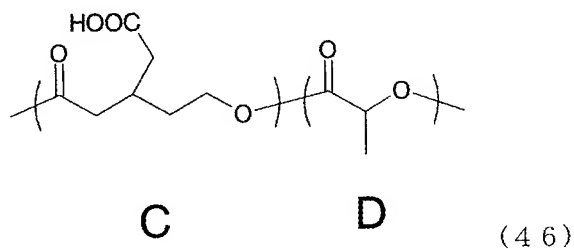
[0233]

5 (Example 16)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and 2-aminobenzenesulfonic acid

10 [0234]

[chemical formula 71]



[0235]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.35 g of 2-aminobenzenesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-

precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.34 g
5 of polymer was obtained by carrying out drying under reduced pressure.

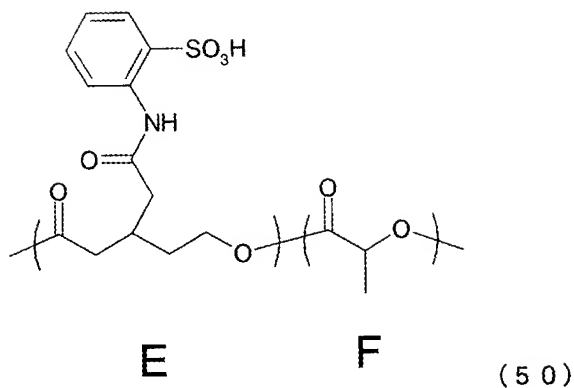
[0236]

The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker
10 DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing
15 IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the peak resulted from the aromatic ring in 2-
20 aminobenzenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (50) as a monomer unit.

[0237]

25 [chemical formula 72]



[0238]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical
 5 formula (50), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0239]

The average molecular weight of the obtained
 10 polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 16,700,
 15 and weight average molecular weight, M_w was 24,700.

[0240]

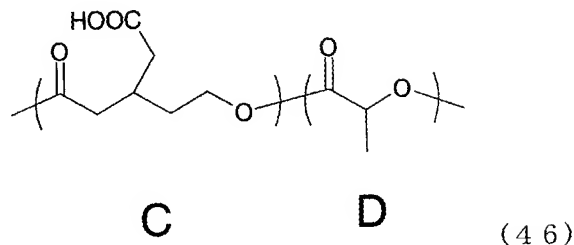
(Example 17)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical
 20 formula (46) synthesized in Example 12 and 4-

aminobenzenesulfonic acid

[0241]

[chemical formula 73]



5 [0242]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in

10 Example 12, 0.35 g of 4-aminobenzenesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-

15 precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.32 g of polymer was obtained by carrying out drying under

20 reduced pressure.

[0243]

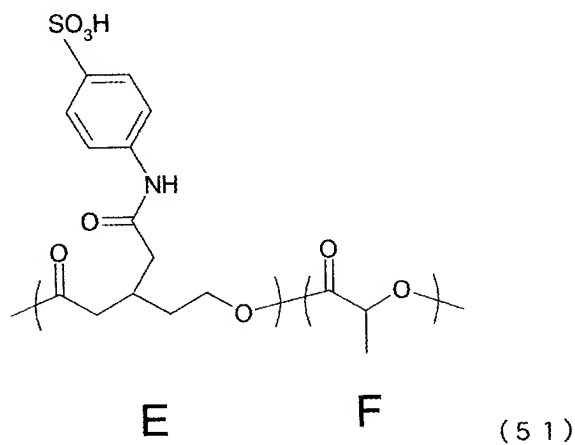
The structure of the obtained polymer was

determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the peak resulted from the aromatic ring in 4-aminobenzenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (51) as a monomer unit.

[0244]

[chemical formula 74]



[0245]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (51), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0246]

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 16,100, and weight average molecular weight, M_w was 24,300.

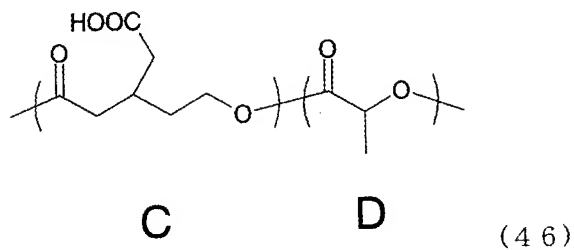
[0247]

(Example 18)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and p-toluidine-2-sulfonic acid

[0248]

[chemical formula 75]



[0249]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical
5 formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.38 g of p-toluidine-2-sulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated
10 at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.35 g
15 of polymer was obtained by carrying out drying under reduced pressure.

[0250]

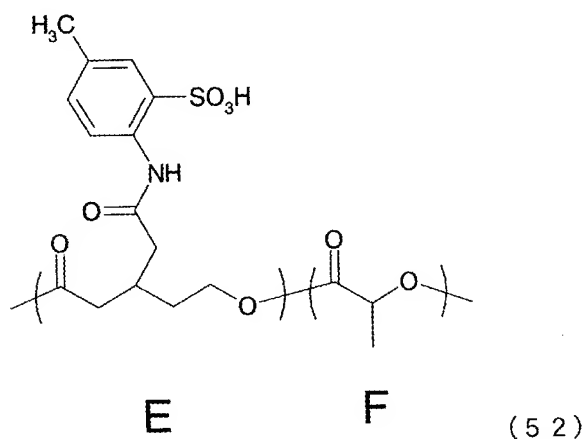
The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker
20 DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing
25 IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of $^1\text{H-NMR}$ showed a shift of the peak resulted from the aromatic ring in p-toluidine-2-sulfonic acid structure and accordingly it was confirmed that the obtained polymer was a

5 polyhydroxyalkanoate containing a unit represented by the following chemical formula (52) as a monomer unit.

[0251]

[chemical formula 76]



10 [0252]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (52), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E

15 and 92 mol % for unit F.

[0253]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer

Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 15,700, and weight average molecular weight, M_w was 24,600.

5 [0254]

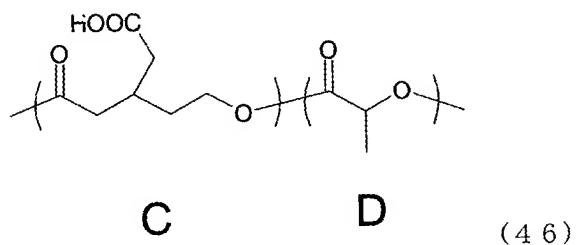
(Example 19)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in Example 12 and 2-aminobenzenesulfonic acid phenyl ester

10

[0255]

[chemical formula 77]



[0256]

15 In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.51 g of 2-aminobenzenesulfonic acid
20 phenyl ester were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and

heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and
5 further washed by agitating in water for one day, and 0.38 g of polymer was obtained by carrying out drying under reduced pressure.

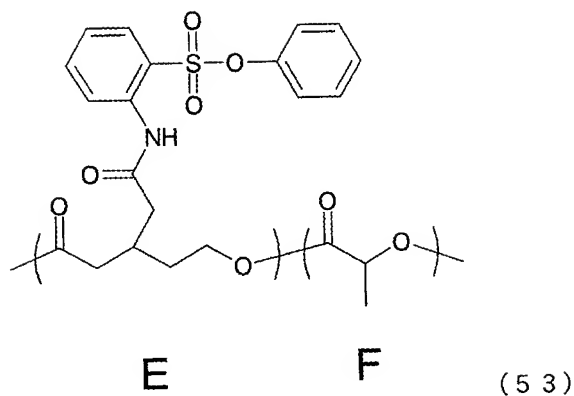
[0257]

The structure of the obtained polymer was
10 determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum
15 (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the
20 peak resulted from the aromatic ring in 2-aminobenzenesulfonic acid phenyl ester structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (53) as
25 a monomer unit.

[0258]

[chemical formula 78]



[0259]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (53), it was confirmed that it was a
 5 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0260]

The average molecular weight of the obtained
 10 polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 17,100,
 15 and weight average molecular weight, Mw was 24,600.

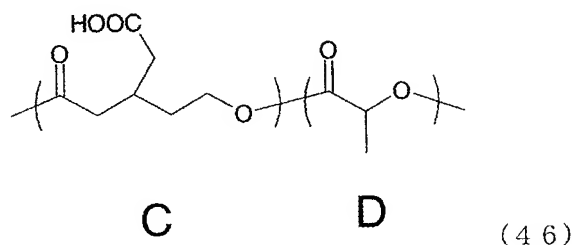
[0261]

(Example 20)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit

represented by chemical formula (46) synthesized in
 Example 12 and 2-amino-1-naphthalenesulfonic acid
 [0262]

[chemical formula 79]



5

[0263]

In a nitrogen atmosphere, 0.40 g of a polymer
 synthesized from the polyhydroxyalkanoate copolymer
 which consists of a unit represented by the chemical
 10 formula (46) (C: 8 mol%, D: 92 mol%) obtained in
 Example 12, 0.45 g of 2-amino-1-naphthalenesulfonic
 acid were added to a 100 ml three-necked flask and
 agitated with 15.0 ml of pyridine added, and then
 1.06 ml of triphenyl phosphite was added and heated
 15 at 120°C for 6 hours. After the reaction ended, re-
 precipitation was performed from 150 ml of ethanol to
 collect the product. The obtained polymer was washed
 with 1N hydrochloric acid for one day and further
 washed by agitating in water for one day, and 0.34 g
 20 of polymer was obtained by carrying out drying under
 reduced pressure.

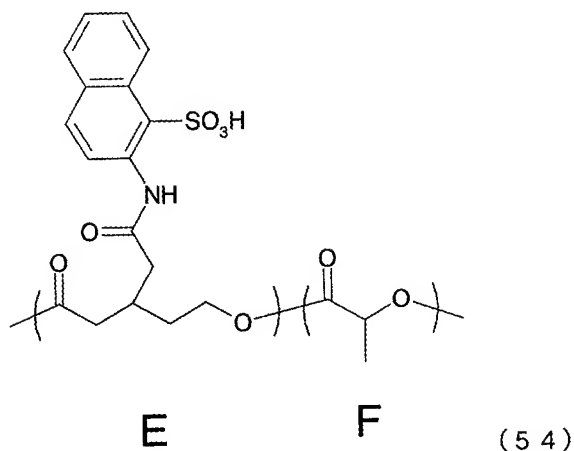
[0264]

The structure of the obtained polymer was determined by analyzing with $^1\text{H-NMR}$ (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of $^1\text{H-NMR}$ showed a shift of the peak resulted from the aromatic ring in 2-amino-1-naphthalenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (54) as a monomer unit.

[0265]

[chemical formula 80]



[0266]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (54), it was confirmed that it was a
5 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol % for unit F.

[0267]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation
10 chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 16,900, and weight average molecular weight, M_w was 25,700.

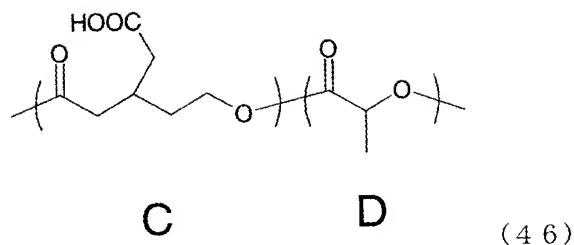
15 [0268]

(Example 21)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (46) synthesized in
20 Example 12 and 2-amino-2-methylpropanesulfonic acid

[0269]

[chemical formula 81]



[0270]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (46) (C: 8 mol%, D: 92 mol%) obtained in Example 12, 0.31 g of 2-amino-2-methylpropanesulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.31 g of polymer was obtained by carrying out drying under reduced pressure.

[0271]

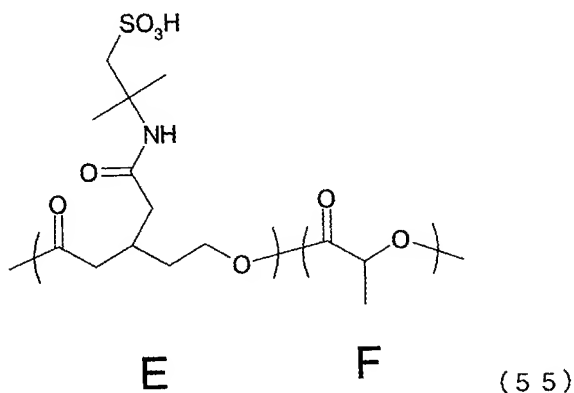
The structure of the obtained polymer was determined by analyzing with ¹H-NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ¹H; solvent used: d-DMSO; measurement

temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from
 5 carboxylic acid decreased, and a peak resulted from amide group at $1,668\text{ cm}^{-1}$ was newly observed.

The results of $^1\text{H-NMR}$ showed a shift of the peak resulted from the methylene of 2-amino-2-methylpropanesulfonic acid structure and accordingly
 10 it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (55) as a monomer unit.

[0272]

[chemical formula 82]



15

[0273]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (55), it was confirmed that it was a
 20 copolymer having a monomer ratio of 8 mol% for unit E

and 92 mol% for unit F.

[0274]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 17,300, and weight average molecular weight, M_w was 24,600.

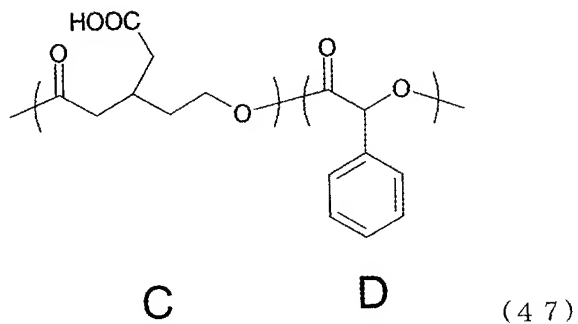
[0275]

(Example 22)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical formula (47) synthesized in Example 13 and 3-aminobenzenesulfonic acid

[0276]

[chemical formula 83]



[0277]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer

which consists of a unit represented by the chemical formula (47) (C: 10 mol%, D: 90 mol%) obtained in Example 13, 0.25 g of 3-aminobenzenesulfonic acid were added to a 100 ml three-necked flask and
5 agitated with 15.0 ml of pyridine added, and then 0.76 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed
10 with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.33 g of polymer was obtained by carrying out drying under reduced pressure.
[0278]

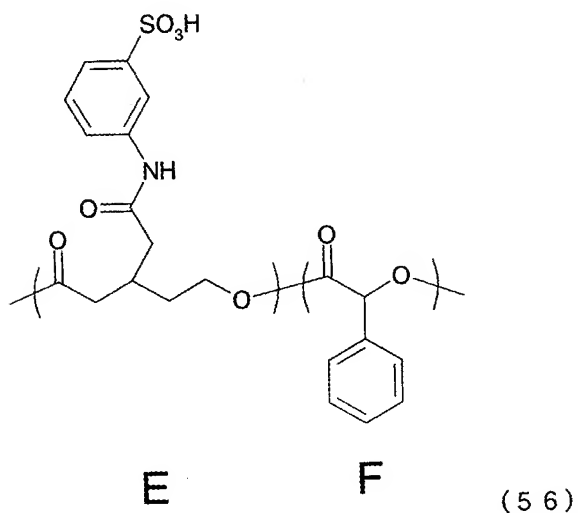
15 The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier
20 transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

25 The results of ^1H -NMR showed a shift of the peak resulted from the aromatic ring of 3-aminobenzenesulfonic acid structure and accordingly

it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (56) as a monomer unit.

[0279]

5 [chemical formula 84]



[0280]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (56), it was confirmed that it was a copolymer having a monomer ratio of 10 mol% for unit E and 90 mol% for unit F.

[0281]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently,

the number average molecular weight, M_n was 13,100,
and weight average molecular weight, M_w was 17,700.

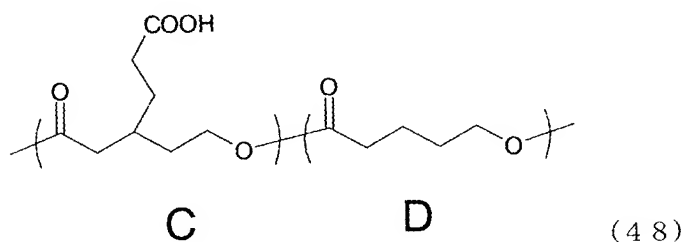
[0282]

(Example 23)

5 Condensation reaction of the
polyhydroxyalkanoate which consist of a unit
represented by chemical formula (48) synthesized in
Example 14 and 4-methoxyaniline-2-sulfonic acid

[0283]

10 [chemical formula 85]



[0284]

In a nitrogen atmosphere, 0.40 g of a polymer
synthesized from the polyhydroxyalkanoate copolymer
15 which consists of a unit represented by the chemical
formula (48) (C: 13 mol%, D: 87 mol%) obtained in
Example 14, 0.48g of 4-methoxyaniline-2-sulfonic acid
were added to a 100 ml three-necked flask and
agitated with 15.0 ml of pyridine added, and then
20 1.24 ml of triphenyl phosphite was added and heated
at 120°C for 6 hours. After the reaction ended, re-
precipitation was performed from 150 ml of ethanol to

collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.37 g of polymer was obtained by carrying out drying under
5 reduced pressure.

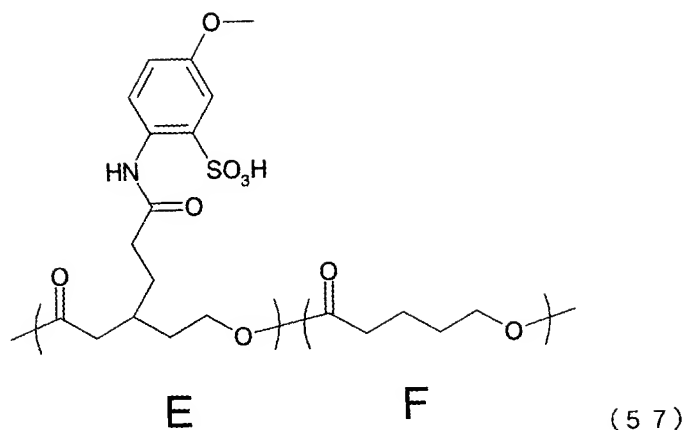
[0285]

The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide
10 measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from
15 carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the peak resulted from the aromatic ring of 4-methoxyaniline-2-sulfonic acid structure and
20 accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (57) as a monomer unit.

[0286]

25 [chemical formula 86]



[0287]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical
 5 formula (57), it was confirmed that it was a copolymer having a monomer ratio of 13 mol% for unit E and 87 mol% for unit F.

[0288]

The average molecular weight of the obtained
 10 polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 14,800,
 15 and weight average molecular weight, M_w was 20,600.

[0289]

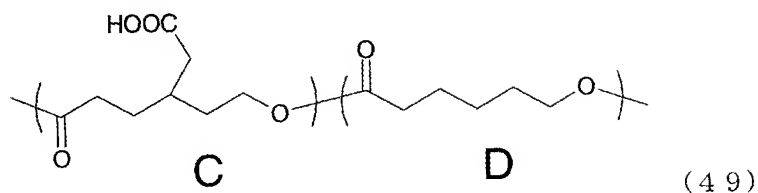
(Example 24)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit

represented by chemical formula (49) synthesized in
Example 15 and taurine

[0290]

[chemical formula 87]



5

[0291]

In a nitrogen atmosphere, 0.40 g of a polymer
synthesized from the polyhydroxyalkanoate copolymer
which consists of a unit represented by the chemical
10 formula (49) (C: 12 mol%, D: 88 mol%) obtained in
Example 15, 0.25 g of taurine were added to a 100 ml
three-necked flask and agitated with 15.0 ml of
pyridine added, and then 1.03 ml of triphenyl
phosphite was added and heated at 120°C for 6 hours.
15 After the reaction ended, re-precipitation was
performed from 150 ml of ethanol to collect the
product. The obtained polymer was washed with 1N
hydrochloric acid for one day and further washed by
agitating in water for one day, and 0.31 g of polymer
20 was obtained by carrying out drying under reduced
pressure.

[0292]

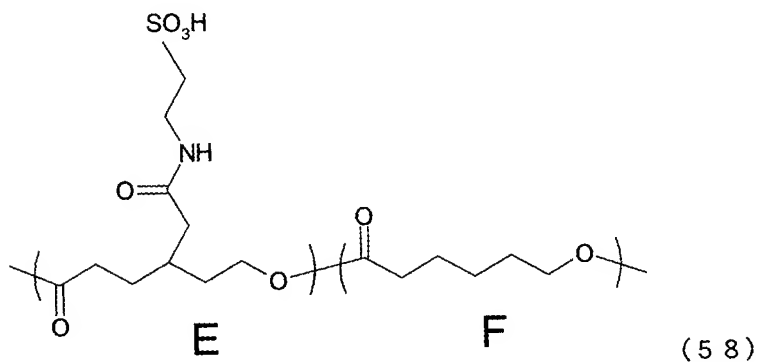
The structure of the obtained polymer was

determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,668\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the peak resulted from the methylene of taurine structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (58) as a monomer unit.

[0293]

[chemical formula 88]



[0294]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical

formula (58), it was confirmed that it was a copolymer having a monomer ratio of 12 mol% for unit E and 88 mol% for unit F.

[0295]

5 The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently,
10 the number average molecular weight, M_n was 15,500, and weight average molecular weight, M_w was 22,200.

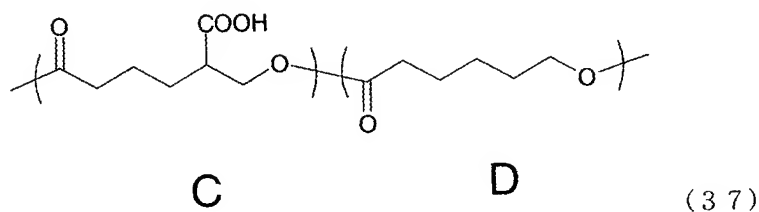
[0296]

(Example 25)

Condensation reaction of polyhydroxyalkanoate
15 which consist of a unit represented by chemical formula (37) synthesized in Example 7 and 2-aminobenzenesulfonic acid

[0297]

[chemical formula 89]



20

[0298]

In a nitrogen atmosphere, 0.40 g of a polymer

synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (37) (C: 14 mol%, D: 86 mol%) obtained in Example 7, 0.40 g of 2-aminobenzenesulfonic acid were
5 added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.21 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the
10 product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.36 g of polymer was obtained by carrying out drying under reduced pressure.

15 [0299]

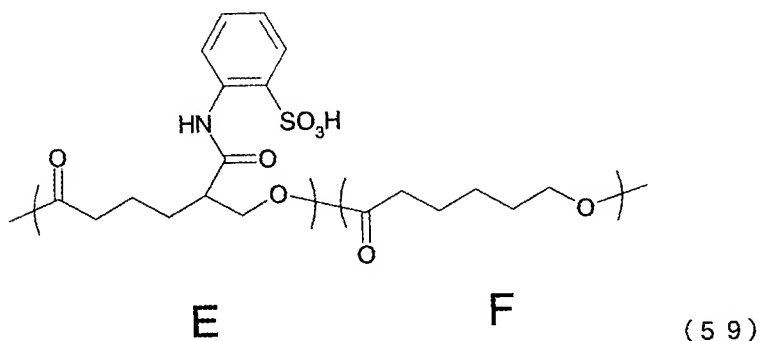
The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement
20 temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from
25 amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the peak resulted from the aromatic ring of 2-

aminobenzenesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (59) as a monomer unit.

5 [0300]

[chemical formula 90]



[0301]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (59), it was confirmed that it was a copolymer having a monomer ratio of 14 mol% for unit E and 86 mol% for unit F.

[0302]

15 The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, 20 the number average molecular weight, M_n was 9,400, and weight average molecular weight, M_w was 13,400.

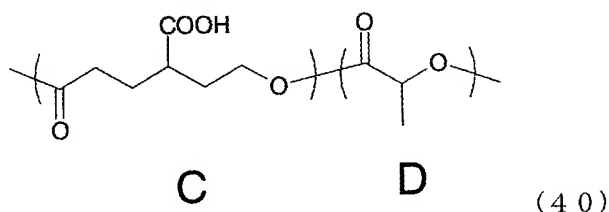
[0303]

(Example 26)

Condensation reaction of the
polyhydroxyalkanoate which consist of a unit
5 represented by chemical formula (40) synthesized in
Example 8 and 2-amino-2-methylpropanesulfonic acid

[0304]

[chemical formula 91]



10 [0305]

In a nitrogen atmosphere, 0.40 g of a polymer
synthesized from the polyhydroxyalkanoate copolymer
which consists of a unit represented by the chemical
formula (40) (C: 8 mol%, D: 92 mol%) obtained in
15 Example 8, 0.31 g of 2-amino-2-methylpropanesulfonic
acid were added to a 100 ml three-necked flask and
agitated with 15.0 ml of pyridine added, and then
1.06 ml of triphenyl phosphite was added and heated
at 120°C for 6 hours. After the reaction ended, re-
20 precipitation was performed from 150 ml of ethanol to
collect the product. The obtained polymer was washed
with 1N hydrochloric acid for one day and further
washed by agitating in water for one day, and 0.33 g

of polymer was obtained by carrying out drying under reduced pressure.

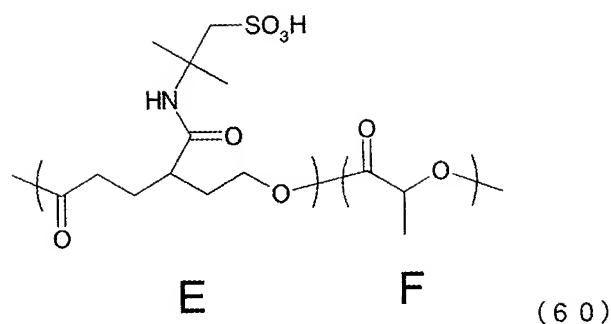
[0306]

The structure of the obtained polymer was
5 determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum
10 (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,668\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the
15 peak resulted from the aromatic ring of 2-amino-2-methylpropanesulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (60) as a monomer unit.

20 [0307]

[chemical formula 92]



[0308]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical
 5 formula (60), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit E and 92 mol% for unit F.

[0309]

The average molecular weight of the obtained
 10 polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 8,100,
 15 and weight average molecular weight, M_w was 12,400.

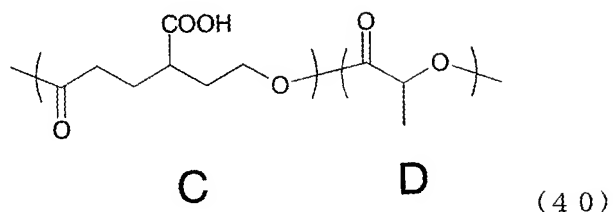
[0310]

(Example 27)

Condensation reaction of polyhydroxyalkanoate which consist of a unit represented by chemical
 20 formula (40) synthesized in Example 8 and 4-aminobenzenesulfonic acid phenyl ester

[0311]

[chemical formula 93]



[0312]

5 In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (40) (C: 8 mol%, D: 92 mol%) obtained in Example 8, 0.51 g of 4-aminobenzenesulfonic acid

10 phenyl ester were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of

15 ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.35 g of polymer was obtained by carrying out drying under reduced pressure.

20 [0313]

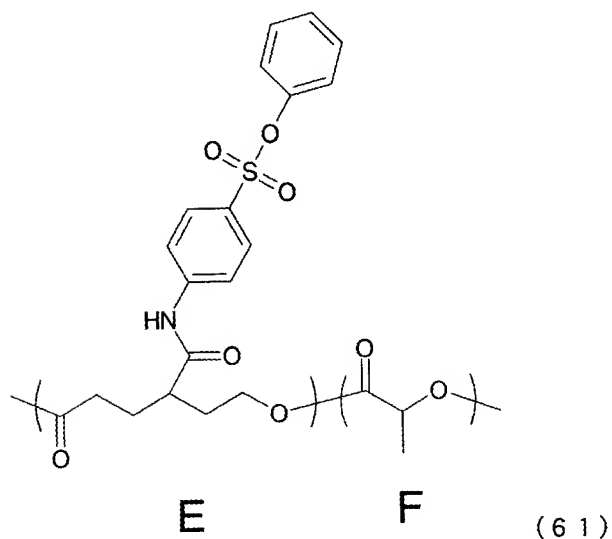
The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide

measured: ^1H ; solvent used: d-DMSO; measurement
 temperature: room temperature) and Fourier
 transformation-infrared absorption (FT-IR) spectrum
 (Nicolet AVATAR360 FT-IR). As a result of performing
 5 IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from
 carboxylic acid decreased, and a peak resulted from
 amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the
 peak resulted from the aromatic ring of 4-
 10 aminobenzenesulfonic acid phenyl ester structure and
 accordingly it was confirmed that the obtained
 polymer was a polyhydroxyalkanoate containing a unit
 represented by the following chemical formula (61) as
 a monomer unit.

15 [0314]

[chemical formula 94]



[0315]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (61), it was confirmed that it was a
 5 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol% for unit F.

[0316]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation
 10 chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 7,800, and weight average molecular weight, Mw was 14,300.

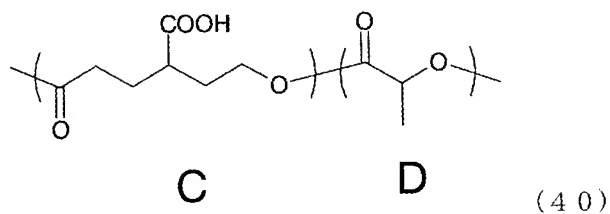
15 [0317]

(Example 28)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (40) synthesized in
 20 Example 8 and 1-naphthylamine-8-sulfonic acid

[0318]

[chemical formula 95]



[0319]

In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical
5 formula (40) (C: 8 mol%, D: 92 mol%) obtained in Example 8, 0.45 g of 1-naphthylamine-8-sulfonic acid were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 1.06 ml of triphenyl phosphite was added and heated
10 at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further washed by agitating in water for one day, and 0.33 g
15 of polymer was obtained by carrying out drying under reduced pressure.

[0320]

The structure of the obtained polymer was determined by analyzing with ^1H -NMR (FT-NMR: Bruker
20 DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum (Nicolet AVATAR360 FT-IR). As a result of performing
25 IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

[chemical formula 96]



As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (62), it was confirmed that it was a
15 copolymer having a monomer ratio of 8 mol% for unit E and 92 mol% for unit F.

The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer

Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 8,200, and weight average molecular weight, M_w was 12,400.

5 [0324]

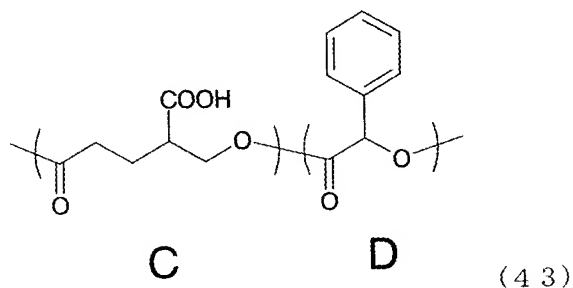
(Example 29)

Condensation reaction of the polyhydroxyalkanoate which consist of a unit represented by chemical formula (43) synthesized in Example 9 and 4-methoxyaniline-2-sulfonic acid

10

[0325]

[chemical formula 97]



[0326]

15 In a nitrogen atmosphere, 0.40 g of a polymer synthesized from the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (43) (C: 7 mol%, D: 93 mol%) obtained in Example 9, 0.21 g of 4-methoxyaniline-2-sulfonic acid

20 were added to a 100 ml three-necked flask and agitated with 15.0 ml of pyridine added, and then 0.54 ml of triphenyl phosphite was added and heated

at 120°C for 6 hours. After the reaction ended, re-precipitation was performed from 150 ml of ethanol to collect the product. The obtained polymer was washed with 1N hydrochloric acid for one day and further
5 washed by agitating in water for one day, and 0.32 g of polymer was obtained by carrying out drying under reduced pressure.

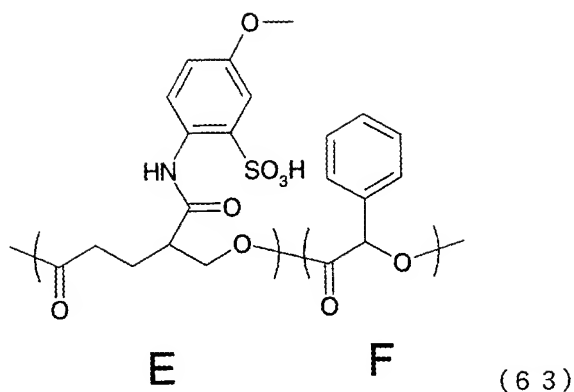
[0327]

The structure of the obtained polymer was
10 determined by analyzing with ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature) and Fourier transformation-infrared absorption (FT-IR) spectrum
15 (Nicolet AVATAR360 FT-IR). As a result of performing IR measurement, the peak of $1,695\text{ cm}^{-1}$ resulted from carboxylic acid decreased, and a peak resulted from amide group at $1,658\text{ cm}^{-1}$ was newly observed.

The results of ^1H -NMR showed a shift of the
20 peak resulted from the aromatic ring of 4-methoxyaniline-2-sulfonic acid structure and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (63) as
25 a monomer unit.

[0328]

[chemical formula 98]



[0329]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical
 5 formula (63), it was confirmed that it was a copolymer having a monomer ratio of 7 mol% for unit E and 93 mol% for unit F.

[0330]

The average molecular weight of the obtained
 10 polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 6,900,
 15 and weight average molecular weight, M_w was 10,100.

[0331]

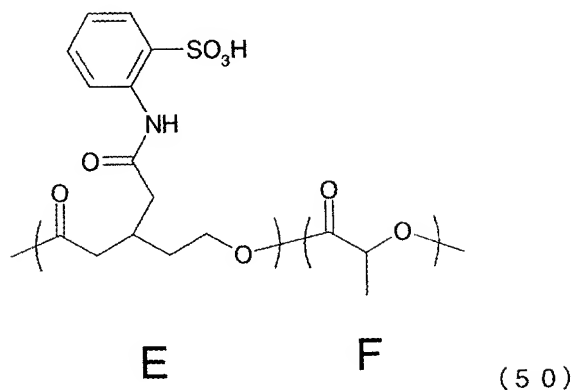
(Example 30)

Esterification reaction of the polyhydroxyalkanoate which consists of a unit
 20 represented by chemical formula (50) synthesized in

Example 16

[0332]

[chemical formula 99]



5 [0333]

0.30 g of the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (50) (E: 8 mol%, F: 92 mol%) obtained in Example 16 was added to an eggplant flask and dissolved with 21.0 ml of chloroform and 7.0 ml of methanol added and cooled to 0°C. 1.31 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution (product of Aldrich) was added to this, and agitated for 4 hours. After the reaction ended, the solvent was removed with an evaporator and the polymer was collected.

15

[0334]

21.0 ml of chloroform, 7.0 ml of methanol were further added to re-dissolve the polymer and the solvent was evaporated by an evaporator. This

20

operation was repeated 3 times.

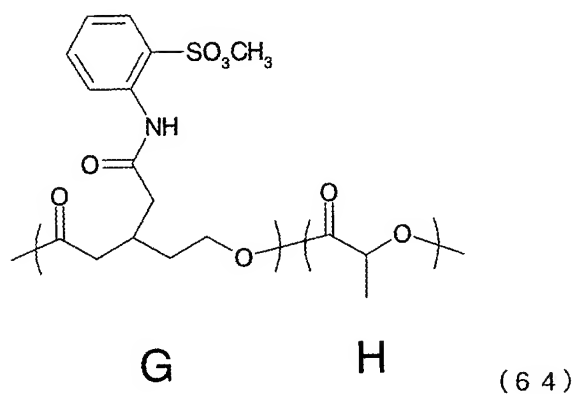
[0335]

0.30 g of the polymer was obtained by drying the polymer collected here under reduced pressure.

5 The determination of the structure of the obtained polymer was performed by ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature). The results of ^1H -
10 NMR showed a peak resulted from methyl sulfonate at 3 to 4 ppm and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (64) as a monomer unit.

15 [0336]

[chemical formula 100]



[0337]

As for the ratio of the units in the
20 polyhydroxyalkanoate represented by the chemical

formula (64), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit G and 92 mol% for unit H.

[0338]

5 In addition, there was no peak observed resulted from sulfonic acid in acid value titration using Potentiometric Titrator AT510 (product of Kyoto Electronics Manufacturing Co., Ltd.) and it was also made evident from this that sulfonic acid was
10 converted to methyl sulfonate.

[0339]

 The average molecular weight of the obtained polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer
15 Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, M_n was 15,900, and weight average molecular weight, M_w was 24,200.

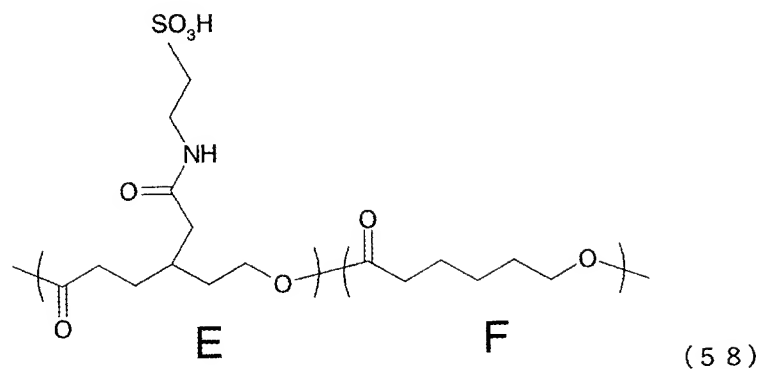
[0340]

20 (Example 31)

 Esterification reaction of the polyhydroxyalkanoate which consists of a unit represented by chemical formula (58) synthesized in Example 24

25 [0341]

[chemical formula 101]



[0342]

0.30 g of the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (58) (E: 12 mol%, F: 88 mol%) obtained in
 5 Example 24 was added to an eggplant flask and dissolved with 21.0 ml of chloroform and 7.0 ml of methanol added and cooled to 0°C. 1.34 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution (product
 10 of Aldrich) was added to this, and agitated for 4 hours. After the reaction ended, the solvent was removed with an evaporator and the polymer was collected.

[0343]

15 21.0 ml of chloroform, 7.0 ml of methanol were further added to re-dissolve the polymer and the solvent was removed by an evaporator. This operation was repeated 3 times.

[0344]

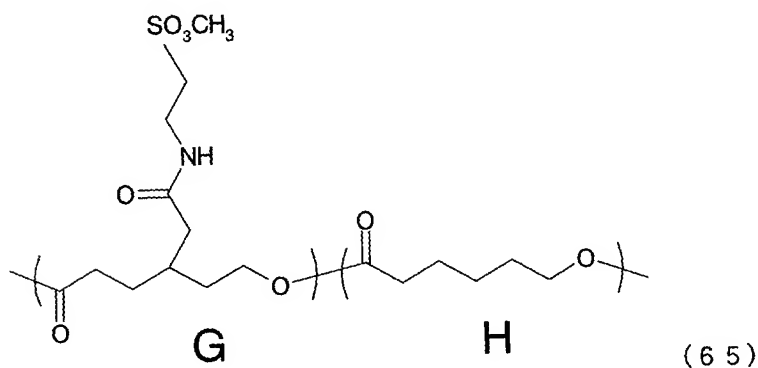
20 0.31 g of the polymer was obtained by drying

the polymer collected here under reduced pressure.

The determination of the structure of the obtained polymer was performed by ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature). The results of ^1H -NMR showed a peak resulted from methyl sulfonate at 3 to 4 ppm and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (65) as a monomer unit.

[0345]

[chemical formula 102]



15 [0346]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (65), it was confirmed that it was a copolymer having a monomer ratio of 12 mol% for unit G and 88 mol% for unit H.

[0347]

In addition, there was no peak observed
resulted from sulfonic acid in acid value titration
using Potentiometric Titrator AT510 (product of Kyoto
5 Electronics Manufacturing Co., Ltd.) and it was also
made evident from this that sulfonic acid was
converted to methyl sulfonate.

[0348]

The average molecular weight of the obtained
10 polymer was estimated by gel permeation
chromatography (GPC; TOSOH, column; Polymer
Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr
0.1% (w/v), polystyrene conversion). Consequently,
the number average molecular weight, Mn was 14,700,
15 and weight average molecular weight, Mw was 21,800.

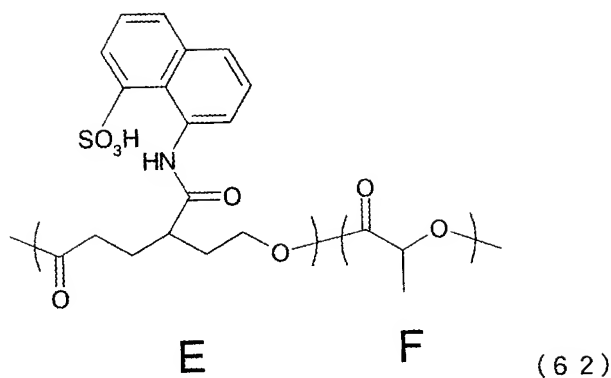
[0349]

(Example 32)

Esterification reaction of the
polyhydroxyalkanoate which consists of a unit
20 represented by chemical formula (62) synthesized in
Example 28

[0350]

[chemical formula 103]



[0351]

0.30 g of the polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical
 5 formula (62) (E: 8 mol%, F: 92 mol%) obtained in Example 28 was added to an eggplant flask and dissolved with 21.0 ml of chloroform and 7.0 ml of methanol added and cooled to 0°C. 1.34 ml of 2 mol/L trimethylsilyldiazomethane-hexane solution (product
 10 of Aldrich) was added to this, and agitated for 4 hours. After the reaction ended, the solvent was removed with an evaporator and the polymer was collected.

[0352]

15 21.0 ml of chloroform, 7.0 ml of methanol were further added to re-dissolve the polymer and the solvent was removed by an evaporator. This operation was repeated 3 times.

[0353]

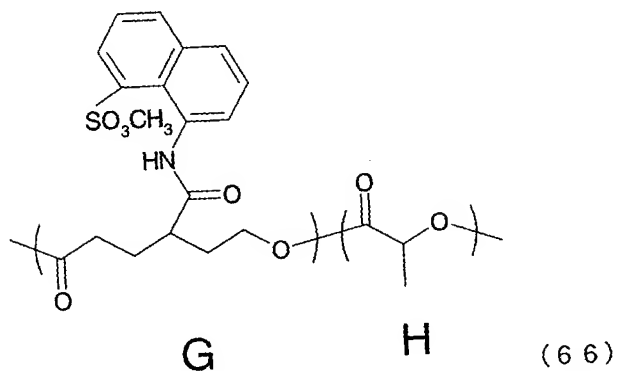
20 0.30 g of the polymer was obtained by drying

the polymer collected here under reduced pressure.

The determination of the structure of the obtained polymer was performed by ^1H -NMR (FT-NMR: Bruker DPX400; resonant frequency: 400 MHz; nuclide measured: ^1H ; solvent used: d-DMSO; measurement temperature: room temperature). The results of ^1H -NMR showed a peak resulted from methyl sulfonate at 3 to 4 ppm and accordingly it was confirmed that the obtained polymer was a polyhydroxyalkanoate containing a unit represented by the following chemical formula (66) as a monomer unit.

[0354]

[chemical formula 104]



15 [0355]

As for the ratio of the units in the polyhydroxyalkanoate represented by the chemical formula (66), it was confirmed that it was a copolymer having a monomer ratio of 8 mol% for unit G and 92 mol% for unit H.

[0356]

In addition, there was no peak observed resulted from sulfonic acid in acid value titration using Potentiometric Titrator AT510 (product of Kyoto
5 Electronics Manufacturing Co., Ltd.) and it was also made evident from this that sulfonic acid was converted to methyl sulfonate.

[0357]

The average molecular weight of the obtained
10 polymer was estimated by gel permeation chromatography (GPC; TOSOH, column; Polymer Laboratories PLgel 5 μ MIXED-C, solvent; DMF/LiBr 0.1% (w/v), polystyrene conversion). Consequently, the number average molecular weight, Mn was 7,500,
15 and weight average molecular weight, Mw was 11,400.

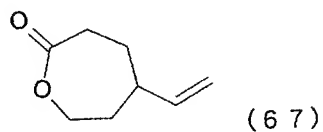
[0358]

(Example 33)

(Synthesis of polyester using 5-ethenyl-2-oxepanone represented by chemical formula (67) and ϵ -
20 caprolactone)

[0359]

[chemical formula 105]



[0360]

0.31 g (2.0 mmol) of 5-ethenyl-2-oxepanone represented by the chemical formula (67), 1.14 g (10.0 mmol) of ϵ -caprolactone, 4.8 ml of 0.01 M toluene solution of tin octylate (tin 2-ethylhexanoate), 4.8 ml of 0.01 M toluene solution of p-tert-butylbenzyl alcohol were placed in a polymerization ampoule and after performing drying under reduced pressure for 1 hour and nitrogen purge, it was heat-sealed under reduced pressure, and heated at 150°C to perform ring-opening polymerization. The reaction was ended after 12 hours and the reaction product was cooled. The obtained polymer was dissolved in chloroform and re-precipitated in methanol in an amount of 10 times of the chloroform required for dissolving the polymer. The precipitation was collected and 0.86 g of polymer was obtained by carrying out drying under reduced pressure.

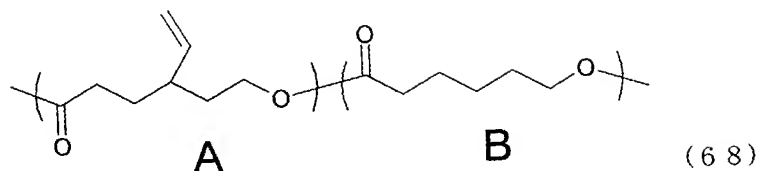
[0361]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate copolymer which contains a unit represented by the following chemical formula (68) as a monomer unit. It was also confirmed that the ratios of monomer units were 12 mol% for A unit and

88 mol% for B unit.

[0362]

[chemical formula 106]



5 [0363]

The average molecular weight of the obtained polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene
 10 conversion). Consequently, the number average molecular weight, M_n was 17,500, and weight average molecular weight, M_w was 25,400.

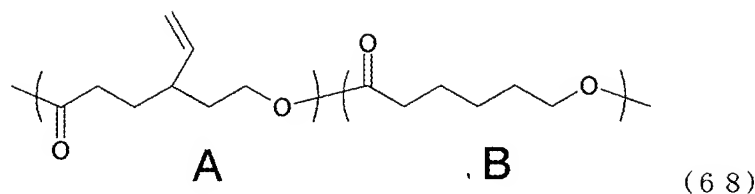
[0364]

(Example 34)

15 Oxidation reaction of polyhydroxyalkanoate which consists of a unit represented by chemical formula (68) synthesized in Example 33

[0365]

[chemical formula 107]



[0366]

0.50 g of a polyhydroxyalkanoate copolymer which consists of a unit represented by the chemical formula (68) (A: 12 mol%, B: 88 mol%) obtained in Example 33 was added to an eggplant flask and dissolved with 30 ml of acetone added. This was placed in an ice bath, and 5 ml of acetic acid and 0.40 g of 18-crown-6-ether were added and the mixture was agitated. Next, 0.32 g of potassium permanganate was slowly added on the ice bath, and agitated in an ice bath for 2 hours, and agitated at room temperature for further 18 hours. 60 ml of ethyl acetate was added after the reaction ended, and 45 ml of water was further added. Next, sodium hydrogen sulfite was added until peracid was removed. Then, the pH of the liquid was adjusted to 1 with 1.0 N hydrochloric acid. The organic layer was extracted and washed 3 times with 1.0 N hydrochloric acid. After the organic layer was collected, crude polymer was collected by evaporating the solvent. Next, polymer was collected, after washed with 50 ml of water, 50 ml of methanol and further with 50 ml of

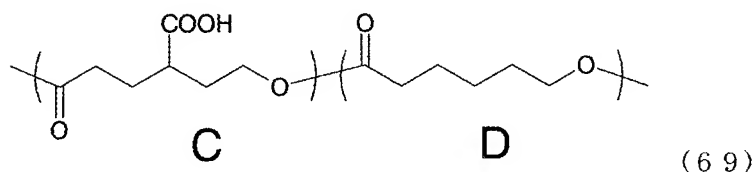
water 3 times. Next, it was dissolved in 3 ml of THF, re-precipitation was performed using methanol in an amount of 50 times of THF required for dissolving the polymer. The precipitation was collected and 0.42 g
 5 of polymer was obtained by carrying out drying under reduced pressure.

[0367]

In order to identify the structure of the obtained polymer, NMR analysis was performed on the
 10 same conditions as in Example 1 and consequently it was confirmed that the obtained compound was a polyhydroxyalkanoate which contains a unit represented by the following chemical formula (69) as a monomer unit.

15 [0368]

[chemical formula 108]



[0369]

The average molecular weight of the obtained
 20 polyhydroxyalkanoate was estimated by gel permeation chromatography (GPC; TOSOH HLC-8220, column; TOSOH TSK-GEL Super HM-H, solvent; chloroform, polystyrene conversion). Consequently, the number average

molecular weight, Mn was 14,300, and weight average molecular weight, Mw was 21,500.

[0370]

In order to calculate the unit of the obtained
5 polyhydroxyalkanoate furthermore, carboxyl groups at
the end of the side chains of the
polyhydroxyalkanoate were subjected to methyl
esterification using trimethylsilyldiazomethane and
the calculation was performed.

10 [0371]

30 mg of the target polyhydroxyalkanoate was
added to 100 ml-volume eggplant flask and dissolved
with 2.1 ml of chloroform and 0.7 ml of methanol
added. 0.5 ml of 2 mol/L trimethylsilyldiazomethane-
15 hexane solution was added to this, and agitated at
room temperature for 1 hour. After the reaction
ended, the solvent was removed and the polymer was
collected. It was washed with 50 ml of methanol and
the polymer was collected after that. 29 mg of
20 polyhydroxyalkanoate was obtained by carrying out
drying under reduced pressure.

[0372]

NMR analysis was performed on the same
conditions as in Example 1 and consequently it was
25 confirmed that the obtained polyhydroxyalkanoate
represented by the chemical formula (69) was a
copolymer having a monomer ratio of 11 mol% for C

unit and 89 mol% for D unit.

[Industrial Applicability]

[0373]

A novel polyhydroxyalkanoate which contains a
5 vinyl group, which is a reactive group, on a side
chain in a molecule, a novel polyhydroxyalkanoate
which contains a carboxyl group in a molecule, a
novel polyhydroxyalkanoate which contains a unit
having an amide group and a sulfonic acid group in a
10 molecule, and a production method thereof are
provided by the present invention. These new
polyhydroxyalkanoates having a vinyl group or a
carboxyl group can have functional groups introduced
therein utilizing these reactive groups, and
15 accordingly can be applied to functional materials.
Furthermore, polyhydroxyalkanoates which contain in a
molecule a carboxyl group and a unit having an amide
group and a sulfonic acid group are excellent in melt
processability, and also excellent in
20 biocompatibility due to their hydrophilicity, and can
be expected to be applied to soft materials for
medical use, etc.

[Document] ABSTRACT

[Abstract]

[Problem to be solved] To provide a novel
polyhydroxyalkanoate having a reactive functional
5 group in a molecule, and a production method thereof,
etc.

[Solution] By utilizing the vinyl group of
polyhydroxyalkanoate which contains a unit having a
vinyl group on a side chain, a polyhydroxyalkanoate
10 which contains a carboxyl group and a unit having an
amide group and a sulfonic acid group in a molecule
is derived.

[Elected drawing] None